

C-H overlap populations for the 2E_1 , 2A_1 , and 1A_1 states are 0.76, 0.71, and 0.67. Thus, the valence orbitals of CH_3O^- have less CH bonding character and hence a longer bond distance. Note that this longer C-H bond distance allows a larger H-H separation, which is particularly significant in the context of the strongly pyramidal methyl group.

The calculated equilibrium SCF energies for the three states were -114.4029 (2E), -114.2711 (2A_1), and -114.3712 (1A_1) hartrees. Thus, the 2A_1 excitation energy T_e is 3.59 eV = 82.7 kcal/mol = $28,900$ cm^{-1} , in good qualitative agreement with the comparable separation¹⁸ in OH, $32,680$ cm^{-1} . The negative ion is predicted to be unstable by 0.86 eV. In fact, of course, CH_3O^- is a relatively stable negative ion, with electron affinity probably comparable to that of OH, 1.83 eV.²¹ This poor result is typical of what should be expected from Hartree-Fock electron affinities,²² since the correlation energy¹¹ of CH_3O^- is significantly greater than that of CH_3O . Interestingly, however, the CH_3O^- Koopmans' theorem ionization potential (2e orbital energy) is 2.02 eV, just about the expected electron affinity of CH_3O .

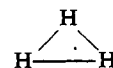
From the Jahn-Teller theorem,²³ it is known that the equilibrium geometry of the methoxy radical must be distorted from C_{3v} in order to eliminate the 2E degeneracy we have assumed thus far. Perhaps the

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simplest way to lower the point group symmetry is by retaining a plane of symmetry while moving the O atom off the line connecting the C atom and the center of the triangle.



Let us call ϕ the angle between the original threefold C-O axis and the new C-O axis. Fixing all other geometrical parameters, including the CO distance, we have carried out calculations for $\phi = 10^\circ$ ($E = -114.3953$), 0° ($E = -114.4029$), and -10° ($E = -114.4004$ hartrees). Note that $\phi = 0^\circ$ corresponds to the earlier predicted C_{3v} equilibrium geometry. Parabolic interpolation suggests a minimum at 2.5° and a final calculation at that point yields $E = -114.4032$ hartrees. Thus, we have verified the existence of a Jahn-Teller distortion for the ground state of CH_3O . The distortion may be described as "staggered," in that the O atom is closer to the two equivalent H atoms than to the third nonequivalent hydrogen. However, this distortion is so small, both in terms of geometry change (2.5°) and energy lowering (0.2 kcal/mole), that it does not seem wise to attach particular significance to it. In fact the real significance of our result lies in the *ab initio* demonstration that for CH_3O , the Jahn-Teller distortion is indeed *small*.

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Free Radicals in an Adamantane Matrix. VIII. Epr and INDO Study of the Benzyl, Anilino, and Phenoxy Radicals and Their Fluorinated Derivatives

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Abstract: We have studied both theoretically by INDO and experimentally by epr the isoelectronic series of radicals benzyl, anilino, and phenoxy and all of their monofluorinated derivatives, in order to study the effect of the different exo groups ($-\text{CH}_2$, $-\text{NH}$, or $-\text{O}$) on the structure and epr parameters of the radicals and to correlate trends in the fluorine and proton hfs with structural changes in the series. Fully optimized geometries calculated by INDO for the parent radicals show that in going from benzyl to phenoxy the benzene ring, which is a distorted hexagon in benzyl, becomes increasingly more symmetric, due to the increasing importance of an ionic resonance form which places an electron pair on the exo atom (C, N, or O) and an unpaired electron on the positively charged ring. Experimentally, we have obtained the epr parameters of all of the monofluoro derivatives of benzyl, anilino, and phenoxy, including those previously unknown. The trends in the various hyperfine splittings show that the overall spin density in the ring is increasing in going from benzyl to phenoxy, thus supporting the prediction of increasing importance of an ionic form, as mentioned above. We have confirmed both experimentally and theoretically the existence of the "ortho" effect in benzyl and anilino but not in phenoxy radicals, whereby the fluorine hfs in *o*-fluoro derivatives is less than would normally be expected. The results suggest that the effect is due to a bonding interaction between the ortho fluorine and a proton on the exo atom.

The benzyl radical has been the subject of many theoretical and experimental investigations, recently summarized by Raimondi, *et al.*,² to study its spin-

density distribution and to test molecular orbital theories. In particular, several groups have recently sug-

(1) ACS-PRF Postdoctoral Fellow.

(2) M. Raimondi, M. Simonetta, and G. F. Tantardini, *J. Chem. Phys.*, **56**, 5091 (1972).

Table I. Experimental Epr Parameters for Benzyl, Anilino, and Phenoxy Radicals and Their Fluorinated Derivatives

Radical	Hyperfine splittings, G ^{a,b}							N	g value ^c	a(para)/ a(ortho)	a _F /a _H
	1	2	3	4	5	6	7				
Benzyl ^d	5.08	1.70	6.00	1.70	5.08	15.7	15.7		2.0025	1.23	
α -Fluorobenzyl	5.25	1.6	6.15	1.6	5.25	17.1	39.7		2.0034	1.17	2.47
<i>o</i> -Fluorobenzyl	5.2	1.85	6.4	1.85	8.2	16.15	16.15		2.0027	1.23	1.54
<i>m</i> -Fluorobenzyl	5.2	1.8	6.3	4.9	5.2	16.0	16.0		2.0027	1.21	2.51
<i>p</i> -Fluorobenzyl	5.3	1.85	14.6	1.85	5.3	16.3	16.3		2.0030		2.33
Anilino ^e	6.0	2.1	8.1	2.1	6.0	14.0		7.8	2.0030	1.35	
<i>o</i> -Fluoroanilino	6.0	2.0	7.55	2.0	12.1	13.6		7.45	2.0035	1.26	2.02
<i>m</i> -Fluoroanilino	6.0	1.8	7.65	5.3	6.0	14.05		7.9	2.0034	1.28	2.50
<i>p</i> -Fluoroanilino	6.0	2.0	19.75	2.0	6.0	13.9		7.8	2.0037		2.43
2,4-Difluoroanilino	5.95	1.9	19.75	1.9	11.85	13.7		7.55	2.0038		1.98, 2.44
Phenoxy	7.4	2.1	9.7	2.1	7.4				2.0055	1.31	
<i>o</i> -Fluorophenoxy	6.3	1.95	9.6	1.95	18.4				2.0054	1.52	2.78
<i>m</i> -Fluorophenoxy	7.9	2.4	8.5	5.8	7.9				2.0052	1.08	2.97
<i>p</i> -Fluorophenoxy	6.9	2.0	26.7	2.0	6.9				2.0055		2.56

^a Numbering as in Figure 1; error ± 0.2 G. ^b The underlined values refer to fluorine, the others to hydrogen. ^c Relative to DPPH = 2.0036; error ± 0.0002 . ^d Determined in adamantane-*d*₁₆ at room temperature. ^e From ref 4.

gested that the calculations on benzyl radical could be improved if the aromatic ring were allowed to distort from a regular hexagon, and both INDO³ and valence bond² calculations have been done making use of this approach. However, to our knowledge, no one has yet calculated a totally energy optimized geometry for the benzyl radical. Also, the anilino and phenoxy radicals, isoelectronic with benzyl, have been the subject of only limited theoretical investigations.⁴⁻⁶

Therefore, fully optimized geometries for the series of radicals benzyl, anilino, and phenoxy would be of considerable interest, both for elucidation of any trends observed in the geometries and for comparison of the unpaired electron-spin densities and epr hyperfine splittings calculated for these "best" geometries with experimental epr data.

Additionally, we have been interested in fluorine hyperfine splittings and wished to investigate both experimentally and theoretically the monofluoro derivatives of this series of radicals. To this end the epr parameters of all monofluoro derivatives of the benzyl, anilino, and phenoxy radicals, including those not previously reported in the literature, and of one difluoro derivative (2,4-difluoroanilino), were obtained in adamantane.

The monofluorobenzyl radicals have been studied by Hudson and coworkers, both experimentally⁷ and theoretically,⁸ and the α,α -difluorobenzyl radical has been investigated recently.^{9,10} Although the anilino radical substituted with bulky groups has been known for some time,¹¹ the unsubstituted anilino radical itself

was only prepared recently by X-irradiation of aniline in an adamantane matrix,⁴ and the fluoroanilino radicals have not been previously reported. The phenoxy radical^{12,13} and many of its derivatives, including the *o*-fluorophenoxy and *p*-fluorophenoxy radicals^{13,14} and some polyfluorinated phenoxy radicals,¹⁴ have been investigated by epr. Kreilick and coworkers^{15,16} have studied some highly substituted fluorinated phenoxy radicals by a combination of nmr in a paramagnetic solvent and epr. However, in spite of the work that has been done, the entire series of monofluorinated radicals has never been considered as a whole.

Experimental Section

The fluorinated aromatic compounds used were obtained from Peninsular Chemical Research, Inc. and used as received. Adamantane (Aldrich Chemical Co.) was purified before use as previously described.¹⁷ The samples were prepared by dissolving adamantane in the appropriate precursor, precipitating the adamantane, and pressing the dried adamantane into a pellet. In the case of phenol and *p*-fluorophenol, which are solid at room temperature, the phenol and adamantane were cosublimed and the solid was then treated as usual.

The samples were X-irradiated at room temperature and the epr spectra obtained with a Varian V-4502 X-band spectrometer, as previously described.¹⁷ The absolute error in the *g* values is ± 0.0002 , but the relative error for the values determined in these experiments is less than ± 0.0001 . Computer simulations of the spectra were compared with the experimental spectra and recomputed if necessary until the best fit was obtained.

The INDO method and its application to hyperfine coupling constants have been described previously.^{6,18,19} In the present study the geometries of the benzyl, anilino, and phenoxy radicals were fully optimized. All parameters were allowed to vary, except that the radicals were assumed to be planar with *C*_{2v} symmetry (ignoring the presence of the anilino NH). These optimized geometries were then used as the skeletons for the calculations on the fluorinated radicals, for which only the C-F bond distances and

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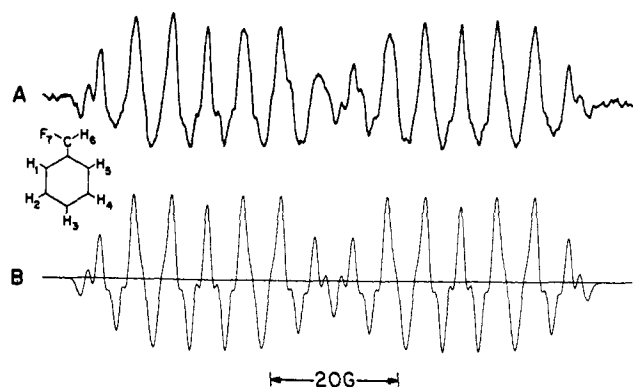


Figure 1. Second-derivative epr spectrum of the radical from X-irradiated α -fluorotoluene in adamantane at room temperature together with a computer simulation based on the parameters of Table I.

C-C-F bond angles were optimized. In the case of the α -fluorobenzyl radical the geometry of the entire -CHF group was optimized. The optimization procedure is similar to that of Gordon and Pople,²⁰ in which the geometric parameters are varied in a stepwise fashion until the total energy is minimized, each step involving optimization of a particular parameter by means of a three-point fit to a parabola. The criterion for the final optimization was self-consistency in total energy to within ± 0.000001 au. During the optimization procedure the INDO spin-density matrix was required to be self-consistent within 1×10^{-4} ; a final run was made at 1×10^{-6} to ensure that the hyperfine splittings were calculated as significantly as possible.

Results

Irradiation of the appropriate precursors in the adamantane matrix gave in all cases results consistent with the formation of a neutral radical by removal of a proton from the substituent group on the benzene ring (-CH₃, -NH₂, or -OH) to give a benzyl radical or one of its isoelectronic analogs anilino or phenoxy. Techniques allowing a choice of abstraction radicals as described here or hydrogen addition radicals from the same precursors have been described recently.²¹ The hyperfine splittings obtained by computer simulation of the experimental spectra are listed in Table I along with the measured *g* values. Assignments of the observed splittings to the individual nuclei were easily made by comparison with the unfluorinated radicals and consideration of the number of equivalent nuclei. The line widths for the fluorobenzyl and fluoroanilino radicals were relatively narrow (~ 1 G), as noted previously for aromatic radicals in adamantane,⁴ but those for the fluorophenoxy radicals were considerably broader. Within the experimental resolution, pairs of protons (methylene, ortho or para) always appeared to be equivalent. Also given in Table I are the ratios $a_{\text{H}}(\text{para})/a_{\text{H}}(\text{ortho})$ and $a_{\text{F}}/a_{\text{H}}$, where a_{H} in the latter case refers to the proton hfs in the unfluorinated parent radical corresponding to the position of fluorine substitution.

Our results for the ring-fluorinated benzyl radicals agree with those obtained by Hudson and Lewis,⁷ who formed the radicals by photolysis of the appropriate fluorotoluene in di-*tert*-butyl peroxide at -70° , although they did not report the *g* values.

Irradiation of α -fluorotoluene in adamantane gave

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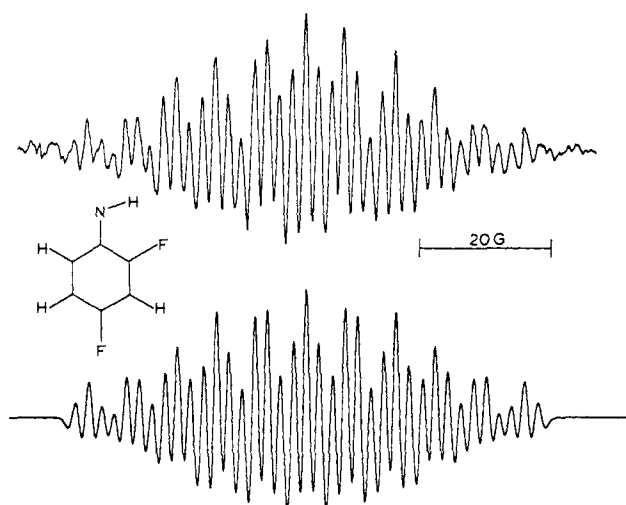


Figure 2. Second-derivative epr spectrum of the radical from X-irradiated 2,4-difluoroaniline in adamantane at room temperature together with a computer simulation based on the parameters of Table I.

the previously unreported α -fluorobenzyl radical, whose spectrum is shown in Figure 1 along with its computer simulation. Somewhat to our surprise, irradiation of benzotrifluoride (C₆H₅CF₃) gave a spectrum identical with that of the α -fluorobenzyl radical rather than the α,α -difluorobenzyl radical^{9,10} that might have been expected. This was probably a result of hydrogen transfer to the initially produced α,α -difluorobenzyl radical to form α,α -difluorotoluene, which then reacted under the continued irradiation to give the observed α -fluorobenzyl radical. Hydrogen exchange between the adamantane matrix and an included radical has been observed previously.²²

The epr parameters of the fluoroanilino radicals are reported here for the first time. A typical second-derivative epr spectrum with its computer simulation based on the data of Table I is shown in Figure 2 for the 2,4-difluoroanilino radical. It is interesting to note that the two fluorine atoms in the same radical do not greatly interact with one another or seriously perturb the system. We have obtained the *m*-fluorophenoxy radical plus the *o*- and *p*-fluorophenoxy radicals previously reported by Stone and Waters.¹³ Our hfs values for the last two radicals differ slightly from those of Stone and Waters¹³ but probably by no more than the stated errors in the two experiments.

In Table II the INDO hyperfine splitting constants calculated for the optimized geometries are tabulated. The $a_{\text{H}}(\text{para})/a_{\text{H}}(\text{ortho})$ and $a_{\text{F}}/a_{\text{H}}$ ratios are also listed for comparison with the experimental values. Where there are two possible para/ortho ratios both are given (as noted above these differences are not resolved experimentally). The C-F bond lengths listed are the final optimized values for each fluorinated radical. The optimized geometries for the benzyl, anilino, and phenoxy radicals and the -CHF group in the α -fluorobenzyl radical are shown in Figure 3. The angles are considered to be reliable to within $\pm 0.2^\circ$ and the bond lengths to within ± 0.002 Å.

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Table II. INDO Results for Optimized Geometries of Benzyl, Anilino, and Phenoxy Radicals and Their Fluorinated Derivatives

Radical	-Hyperfine splittings, G ^{a,b}							X ^c	C-F bond length, Å	a(para)/a(ortho)	a _F /a _H
	1	2	3	4	5	6	7				
Benzyl	-7.18	4.19	-6.68	4.19	-7.18	-17.34	-17.34	32.22 (C)	1.340	0.930	2.82
α-Fluorobenzyl	-6.59	3.81	-6.13	3.88	-6.65	-17.63	-48.87	31.18	1.354	0.923	1.83
o-Fluorobenzyl	-7.36	4.27	-6.79	4.12	<u>13.16</u>	-17.28	-17.25	31.71	1.355	0.907, 0.921	1.73
m-Fluorobenzyl	-7.18	4.29	-6.61	<u>-7.26</u>	<u>-7.29</u>	-17.34	-17.38	32.17	1.354		2.26
p-Fluorobenzyl	-7.28	4.18	15.11	4.18	-7.28	-17.23	-17.23	31.93	1.354		2.26
Anilino	-5.35	3.06	-4.78	3.13	-5.52	-20.46		11.94 (N)		0.893, 0.866	
o-Fluoroanilino (cis)	-5.47	3.12	-4.83	3.04	<u>9.46</u>	-20.32		11.95	1.354	0.883	1.71
o-Fluoroanilino (trans)	<u>11.30</u>	2.94	-4.83	3.18	-5.65	-20.31		12.01	1.353	0.855	2.11
m-Fluoroanilino	-5.53	3.15	-4.74	<u>-5.87</u>	-5.45	-20.51		11.95	1.355	0.857, 0.870	1.88
p-Fluoroanilino	-5.44	3.07	<u>10.62</u>	3.13	-5.56	-20.37		11.91	1.354		2.22
2,4-Difluoroanilino	-5.54	3.06	<u>10.71</u>	2.97	<u>9.59</u>	-20.24		11.93	1.354		2.24, 1.74
Phenoxy	-4.43	2.33	-3.71	2.33	-4.43			14.23 (O)		0.837	
o-Fluorophenoxy	-4.55	2.38	-3.73	2.20	<u>9.22</u>			14.22	1.352	0.820	2.08
m-Fluorophenoxy	-4.46	2.41	-3.68	<u>-5.25</u>	4.51			14.25	1.355	0.825, 0.816	2.25
p-Fluorophenoxy	-4.47	2.36	<u>8.20</u>	2.36	-4.47			14.17	1.354		2.21

^a Numbering as in Figure 1. ^b The underlined values refer to fluorine, the others to hydrogen. ^c X refers to the exo atom, either C, N or O.

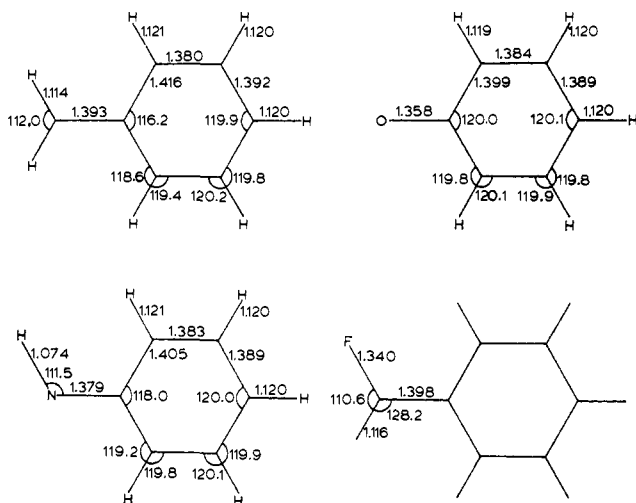


Figure 3. Parameters calculated by INDO for the minimum energy geometries of the benzyl, anilino, and phenoxy radicals and the -CHF group of the α-fluorobenzyl radical.

Discussion

Fluorine Hyperfine Splittings. There have been numerous attempts in the literature to relate fluorine hyperfine splittings to spin densities in fluorine-containing organic radicals, with the hope of obtaining an equation as successful as the McConnell relation for protons. Equations are of the general form

$$a_F = \sum_{ii} Q_{ii}^F \rho_{ii} \quad (1)$$

where Q represents a proportionality constant relating the spin density ρ in molecular orbital ii to the fluorine hfs a_F . One-, two-, and three-term equations have been developed, with the Q parameters being obtained empirically from observed fluorine hfs and estimated spin densities. The various Q parameters thus obtained show a quite wide variation and usually have only

limited usefulness. They are summarized to date by Konishi and Morokuma.²³

There have, however, been several attempts to derive the Q 's theoretically, which would offer some greater hope of generality, since the values so obtained would not depend on the properties of any particular radicals.^{14,23-25} The fluorine hfs values have been calculated by the various theoretical equations for the fluorobenzyl radicals and compared with experiment,^{8,23} with the result that all of them agreed with experiment to about the same degree. We ourselves used the π -orbital spin densities from the INDO programs and the three-parameter equations of Hinchliffe and Murrell,²⁴ Schastnev, *et al.*,^{14,25} and Konishi and Morokuma (both eq 23 and 24 of their paper)²³ to calculate a_F for all of our radicals. We found that they all reproduced the experimental data with about the same reliability as INDO itself (from s-orbital spin density), except for the equation of Hinchliffe and Murrell which gave considerably poorer results. Thus, as we have said before,⁴ it seems likely that Q values are not numbers of great theoretical or practical significance when the atom is included in a π system. For those who wish to make use of our data, we have tabulated in Table III the π -orbital spin densities calculated by INDO for all of the radicals.

It is of interest to note the existence of an "ortho" effect in the fluorine hfs of each series of fluorinated radicals. That is, the ratio a_F/a_H (Table I) is lower for the *o*- than for the *m*- or *p*-fluorinated radicals in the benzyl and anilino series, although it is higher in the phenoxy radicals. Anticipating the discussion in the next section on the INDO calculations, we wish to comment on the INDO results for the cis and trans conformers of the *o*-fluoroanilino radical (Table II).

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Table III. π -Orbital Spin Densities Calculated by INDO for Benzyl, Anilino, and Phenoxy Radicals and Their Fluorinated Derivatives

Radical	Carbon atoms ^a						X ^b	F	C-F ^c
	1	2	3	4	5	6			
Benzyl	-0.1840	0.2576	-0.1489	0.2529	-0.1489	0.2576	0.7138		
α -Fluorobenzyl	-0.1763	0.2368	-0.1376	0.2313	-0.1379	0.2367	0.6760	0.0710	-0.2196
<i>o</i> -Fluorobenzyl	-0.1870	0.2582	-0.1514	0.2522	-0.1526	0.2517	0.7061	0.0226	-0.0775
<i>m</i> -Fluorobenzyl	-0.1854	0.2612	-0.1509	0.2578	-0.1461	0.2630	0.7125	-0.0121	0.0440
<i>p</i> -Fluorobenzyl	-0.1865	0.2569	-0.1518	0.2469	-0.1518	0.2569	0.7073	0.0229	-0.0773
Anilino	-0.1669	0.1902	-0.1127	0.1785	-0.1126	0.1902	0.8333		
<i>o</i> -Fluoroanilino (cis)	-0.1695	0.1894	-0.1141	0.1774	-0.1150	0.1856	0.8290	0.0172	-0.0585
<i>o</i> -Fluoroanilino (trans)	-0.1693	0.1853	-0.1149	0.1773	-0.1139	0.1892	0.8288	0.0176	-0.0590
<i>m</i> -Fluoroanilino	-0.1696	0.1941	-0.1149	0.1827	-0.1109	0.1940	0.8340	-0.0093	0.0337
<i>p</i> -Fluoroanilino	-0.1697	0.1906	-0.1147	0.1739	-0.1150	0.1895	0.8290	0.0164	-0.0553
2,4-Difluoroanilino	-0.1702	0.1884	-0.1131	0.1702	-0.1166	0.1821	0.8259	0.0170	-0.0576
								0.0162	-0.0543
Phenoxy	-0.1422	0.1486	-0.0891	0.1373	-0.0891	0.1486	0.8859		
<i>o</i> -Fluorophenoxy	-0.1432	0.1470	-0.0898	0.1361	-0.0908	0.1447	0.8818	0.0142	-0.0472
<i>m</i> -Fluorophenoxy	-0.1541	0.1523	-0.0912	0.1409	-0.0879	0.1515	0.8871	-0.0075	0.0269
<i>p</i> -Fluorophenoxy	-0.1447	0.1487	-0.0909	0.1339	-0.0909	0.1487	0.8823	0.0129	-0.0431

^a Numbering starts at the bridgehead carbon. The carbon to which fluorine is attached is underlined. ^b X refers to the exo atom, either C, N, or O. ^c C-F refers to the overlap π -orbital spin density in the bond between the fluorine atom and the carbon to which it is attached.

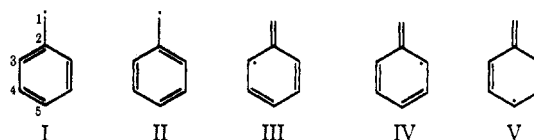
It can be seen that the fluorine hfs and the ratio a_F/a_H are considerably lower for the cis form, where an ortho effect could occur, than for the trans form. Also, INDO predicts that the cis form is more stable by 0.83 kcal than the trans form. Thus, our theoretical and experimental results suggest that there is a bonding interaction between the ortho fluorine and the proton on the exo atom and that this can account for the ortho effect.

Anomalously low *o*-fluorine splittings have been noted previously by Kulkarni and Trapp²⁶ for fluorinated triphenylmethyl radicals and fluorinated benzophenone anion radicals and by Hudson and Lewis⁷ for fluorinated benzaldehyde and nitrobenzene anion radicals. The former authors ascribe the effect to a direct interaction between the *o*-fluorine atom and the "external" carbon atom. Although such a mechanism would imply an ortho effect in the *o*-fluorophenoxy radical also, the fact that it is not observed in this radical is probably due to the relatively large distance between the oxygen and the fluorine.

Although the α -fluorobenzyl radical has not been studied before, several groups have recently investigated the α,α -difluorobenzyl radical.^{9,10} Kispert, *et al.*,⁹ obtained an α -fluorine hfs of 51.4 G and suggested on the basis of both the small size of this splitting when compared with other α -fluoro radicals and INDO calculations of the equilibrium geometry that the radical was planar. By comparison, our value of 39.7 G for the fluorine hfs in α -fluorobenzyl strongly supports a planar geometry, as does the fact that the α -proton hfs of 17.1 G is almost unchanged from benzyl, which is certainly planar.

INDO Geometries. To the best of our knowledge optimized geometries have not previously been reported for the anilino and phenoxy radicals, but there have been many studies on benzyl radical² and several limited INDO calculations on anilino radical.^{4,5} In regard to benzyl, estimation of the bond orders from examination of the resonance structures (I-V below) suggests that the aromatic ring should be distorted from a regular

(26) S. V. Kulkarni and C. Trapp, *J. Amer. Chem. Soc.*, **92**, 4801, 4809 (1970).



hexagon toward a quinoid-like structure, with (referring to the numbering scheme above) r_{12} and r_{34} being shorter than the usual aromatic C-C bond and r_{23} and r_{45} longer. Several recent calculations have made use of such a distorted ring to considerably improve the agreement of calculated proton hfs with experiment.^{2,3}

Our fully optimized INDO geometry for benzyl radical shows this trend toward a quinoid-like structure. The bond lengths are similar to those of Beveridge and Guth^{3a} and to those of Kispert, *et al.*, who calculated INDO geometries for a series of α,α -difluorobenzyl radicals.⁹ The ring angles are the same as those of Raimondi, *et al.*,² but our C-C bond lengths are generally shorter and the total energy of our geometry is 11.0 kcal lower than the energy of the Raimondi, *et al.*, geometry calculated by INDO. The C-H bond lengths and angles were also refined in our calculation. The C-H bond lengths increased significantly from the INDO "standard geometry" distance of 1.08 Å.²⁷ The ring C-H bond angles did not deviate appreciably from the bisectors of the exterior angles, but the methylene proton HCH angle closed to 112°.

The calculated $a(\text{para})/a(\text{ortho})$ ratio for our optimized geometry (0.930) is almost the same as that of Beveridge and Guth^{3a} (0.927), who optimized only the carbon skeleton. It is interesting to note that Raimondi's geometry, which, as mentioned above, is not the minimum energy geometry in the INDO approximation, nevertheless, gives a better $a(\text{para})/a(\text{ortho})$ ratio (0.969). This serves to emphasize the point that attempts to use INDO to exactly fit experimental hyperfine splittings should be viewed with caution.

The geometries of the anilino and phenoxy radicals (Figure 3), when compared with that of benzyl radical, show a trend toward a more symmetric ring. That is, the ring C-C bonds become more nearly the same and

(27) Reference 6, p 131.

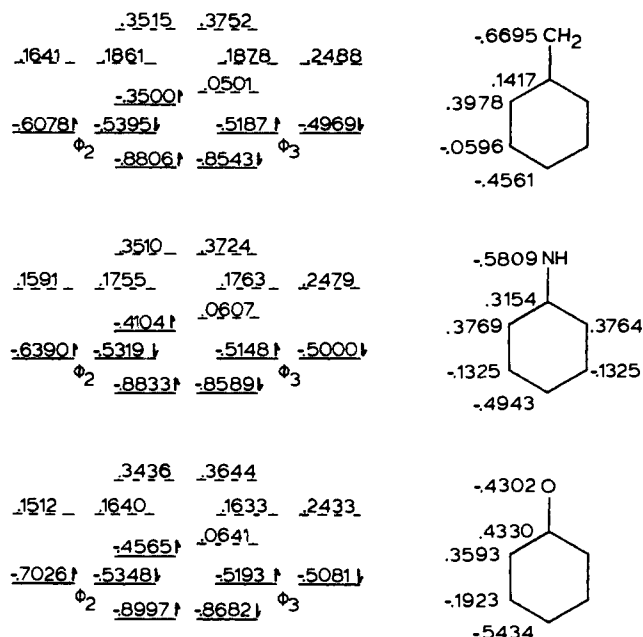
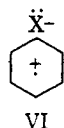


Figure 4. Molecular orbital scheme with the orbital energies calculated by INDO for the α -electron (\uparrow) and β -electron (\downarrow) orbitals for the benzyl, anilino, and phenoxy radicals, together with the orbital coefficients of the highest occupied orbitals.

the ring angles approach 120° . The valence bond resonance structures (I–V above) do not offer any explanation unless an ionic form (VI) is included. This



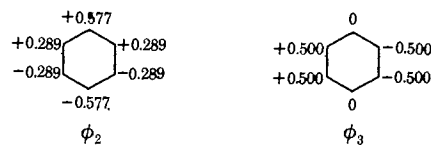
form would imply a fully symmetric ring and would be expected to become more important as X becomes more electronegative. As we go down the series X = C, N, and O, it does of course become more electronegative; furthermore, the valence electron populations calculated by INDO for the three radicals are benzyl methylene carbon = 4.02, anilino nitrogen = 5.19, and phenoxy oxygen = 6.22. The excess electron populations for the last two radicals clearly support the idea of a resonance form that includes a charge separation.

Our calculated structure for the α -fluorobenzyl radical is quite similar to that of Kispert, *et al.*, for the α,α -difluorobenzyl radical, who found a planar structure with $r(C_\alpha-F) = 1.34 \text{ \AA}$ and $r(C_\alpha-C) = 1.40 \text{ \AA}$, essentially the same values as ours.⁹

Spin-Density Distribution and Structure. Comparison of the proton hfs in the series benzyl, anilino, and phenoxy radical and of the fluorine hfs in the fluoro derivatives (Table I) shows that the hyperfine splitting for a substituent at a given position increases as one goes from benzyl to phenoxy, except for the meta proton hfs which are much smaller than the other splittings and remain roughly constant. If it is accepted that the proton hfs is proportional to the spin density on the adjacent carbon and that fluorine substitution does not seriously perturb the rest of the system,⁷ then obviously the total unpaired electron-spin density on the ring is increasing on going from benzyl to phenoxy. This situation is exactly what would be expected as a result of the increasing importance of the ionic res-

onance form (*vide supra*) and the concomitant increasing charge separation between the ring and the hetero group.

Since there seems to be ample experimental evidence for the redistribution of spin density required by the ionic form, we wish now to determine if the INDO calculations support it also. Such a symmetric cationic structure would have an electronic structure similar to that of the benzene radical cation, so that the unpaired electron orbital would be like one of the two degenerate e_1 orbitals of benzene, which are shown below together with their orbital coefficients.²⁸



In the present radicals the degeneracy would of course be lifted by the presence of the hetero group. We have shown in Figure 4 the π -system orbitals along with their energies calculated by INDO for the three radicals. Although in the unrestricted Hartree-Fock formalism used by INDO the α and β electrons are treated separately to obtain one-electron orbitals which strictly speaking cannot be paired up, we have, for the purpose of comparison with the conventional two-electron scheme, arranged the α - and β -electron orbitals in pairs with similar energies. Also given in Figure 4 are the π -orbital coefficients of the highest occupied orbital (always an α -electron orbital in the INDO program) for each radical. For each of the radicals the orbital "pair" marked ϕ_2 has orbital coefficients like those of the benzene ϕ_2 orbital shown above and similarly for ϕ_3 . It can be seen in Figure 4 that ϕ_2 and the half-filled orbital decrease in energy and move closer together in going from benzyl to phenoxy, while ϕ_3 remains about the same in energy. We suggest that the trends are caused by increased mixing between the half-filled orbital from the hetero atom, which comes in at lower and lower energies in the series, C, N, and O, and the ϕ_2 benzene-like orbital. The ϕ_2 orbital is thereby lowered in energy and the half-filled orbital is raised in energy from its "isolated" value, so that it increasingly assumes the characteristics of ϕ_2 , as shown by the decreasing (absolutely) orbital coefficients on the hetero atom (Figure 4).

Conclusions

Comparison of the INDO fully optimized minimum energy geometries for the isoelectronic series of radicals benzyl, anilino, and phenoxy shows that the aromatic ring becomes more nearly a regular hexagon in going from benzyl to phenoxy. At the same time, the half-filled orbital assumes more and more of the characteristics of the ϕ_2 orbital of benzene, as shown by the calculated orbital coefficients for each radical. Taken together these facts suggest that an ionic structure, with the positive charge on the ring, is becoming increasingly important in the series from benzyl to phenoxy.

Experimentally, we have obtained the epr parameters of the monofluoro derivatives of benzyl, anilino, and phenoxy that were previously unknown, so that, in conjunction with published results, epr data for the com-

(28) R. Daudel, R. Lefebvre, and C. Moser, "Quantum Chemistry Methods and Applications," Interscience, New York, N. Y., 1959, p 448.

plete series are now available. Examination of the trends of the various hyperfine splittings shows that the overall spin density on the ring is increasing in going down the series. Thus, the epr data on both the parent radicals and their monofluoro derivatives support the hypothesis that an ionic resonance form with a symmetric aromatic ring is important in explaining the structure of these radicals.

We have confirmed both experimentally and theoretically the existence of the "ortho" effect in benzyl and anilino radicals, whereby the fluorine hfs in *o*-fluorinated

radicals is smaller than would normally be expected. Our results suggest that when a proton is present on the exo group this effect is due to hydrogen bonding between the proton and the fluorine.

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The Electronic Spectra of Nucleic Acid Bases. II. Out-of-Plane Transitions and the Structure of the Nonbonding Orbitals

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Abstract: The energies of the lower out-of-plane transitions of nucleic acid bases and their tautomers and ions are calculated with the CNDO-CI method, which includes all valence electrons. Precise values are obtained by using the energy differences between the observable $\pi\pi^*$ transitions and the $n\pi^*$ transitions, instead of calculating absolute values, and by correcting them empirically for systematic deficiencies of the MO-CI model applied. The $n\pi^*$ transitions of the various bases are characterized and correlated by their transition densities. This reveals that the lowest $n\pi^*$ state bears a close relation to the structure and energy of the highest nonbonding orbital. The structure of the nonbonding orbitals of interest can also be rationalized in simple terms. From the structure of the lowest $n\pi^*$ state and the highest nonbonding orbital it is shown that the bases naturally fall into three classes with respect to their low-energy out-of-plane spectra. The first, which we call the pyrimidine class, comprises the bases without a carbonyl group. The lower $n\pi^*$ transitions are located on nitrogen atoms of the six-membered ring of the bases and have a structure similar to those of pyrimidine. The second, or carbonyl class, consists of the bases containing a carbonyl group with no heteroatom with a lone pair of σ electrons next to it. The lowest $n\pi^*$ transitions are confined largely to the carbonyl oxygen and strongly resemble that of cyclohexanone. The third class is intermediate to the other two, and the bases belonging to it have a nitrogen atom with a lone pair of σ electrons next to a carbonyl group. The two lowest $n\pi^*$ states are mainly spread out over this fragment of the molecule. Their energy is lower than for the corresponding tautomers belonging to the carbonyl class. From the structure of the $n\pi^*$ transitions the energetic shifts occurring upon structural alterations and the formation of ions can readily be understood. The introduction of an amino or hydroxyl group in α position to the location of a transition leads to a strong blue shift. For this reason, the lowest $n\pi^*$ transition in adenine is shifted in energy above the lowest $\pi\pi^*$ transition, whereas in purine the $n\pi^*$ transition is lowest in energy. For no neutral nucleic acid base is the $n\pi^*$ transition calculated to be lower in energy than the first $\pi\pi^*$ transition. Protonation of the nucleic acid bases often does not affect the structure of a $n\pi^*$ transition. In such a case a *red shift* rather than a blue shift occurs. For deprotonation the opposite is true. Both findings show that the generally accepted conclusions drawn from small chromophores are not necessarily valid for larger ones containing several heteroatoms.

In the preceding paper I¹ we have interpreted the in-plane spectra of nucleic acid bases and their tautomers and ions with the aid of all valence electron MO-CI calculations. These spectra comprise the $\pi\pi^*$ and $\sigma\sigma^*$ transitions, the latter mainly of $n\sigma^*$ character. They are in general intense, except where forbidden by reasons of molecular or local symmetry, and determine therefore the gross appearance of the uv spectra of the bases. The high intensity of many in-plane transitions is a natural consequence of the large dimension of the chromophore in the π plane. Perpendicular to this plane the dimension is much smaller, and the out-of-plane transitions, particularly the $n\pi^*$

transitions dealt with in this paper, therefore, are of much lower intensity. Where out-of-plane transitions are not well separated energetically from intense in-plane transitions, they cannot be observed by simple absorption spectroscopy. Some out-of-plane transitions appearing at higher energy and probably of $\pi\sigma^*$ type have been inferred from single-crystal absorption and reflection spectra.^{2,3} Fluorescence measurements⁴ and the complicated nature of the CD spectra of mononucleosides⁵ as well as perturbations observed in elec-

(2) W. A. Eaton and T. P. Lewis, *J. Chem. Phys.*, **53**, 2164 (1970).

(3) L. B. Clark, private communication.

(4) P. R. Callis, E. J. Rosa, and W. T. Simpson, *J. Amer. Chem. Soc.*, **86**, 2292 (1964).

(5) W. Voelter, R. Records, E. Bunnenberg, and C. Djerassi, *J. Amer. Chem. Soc.*, **90**, 6163 (1968).

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