On Fluorine-19 Hyperfine Splittings in the Electron Spin Resonance Spectra of Fluorinated Aromatic Free Radicals. III. Benzophenone Anion Radicals[1]

Shrikant V. Kulkarni and Charles Trapp[2]

*Contribution from the Department of Chemistry, Illinois Institute of Technology,
Chicago, Illinois 60616, and the Department of Chemistry,
University of Louisville, Louisville, Kentucky 40208.* *Received October 20, 1969*

Abstract: The electron spin resonance spectra of a series of electrolytically generated, fluorine-substituted benzophenone anion radicals have been obtained. The fluorine-19 hyperfine interactions have been satisfactorily correlated with the calculated electron spin densities with use of the two parameters, $Q_{CF}^{F} = -85$ G and $Q_{FC}^{F} = +1043$ G, obtained in part II (the preceding article). The fact that the hyperfine splitting constants obtained from the electron spin resonance spectra of the fluorine-substituted benzophenone anion radicals can be accounted for with these two parameters supports the contention that these two parameters may be generally valid for all fluorine hyperfine splittings in aromatic free radicals.

In the preceding article (part II),[1a] we have suggested that the two-parameter equation (eq 2 of II) originally proposed by Eaton, *et al.*,[3] adequately describes the fluorine-19 hyperfine splittings (hfs) in fluorinated triphenylmethyl radicals. In order to test the general applicability of the two-parameter equation and the accuracy of the magnitudes of the parameters obtained in part II, it was desirable to attempt to correlate the data on another series of radicals with the same parameters as those determined in part II. We have chosen for study a series of fluorinated benzophenone anion radicals. The reasons for this choice are: (1) the electron spin resonance (esr) spectrum of only one other fluorine-substituted benzophenone anion has previously been reported,[4] (2) the benzophenone anion radicals are considerably different from the triphenylmethyl radicals of part II, and thus provide a fair test, and (3) the unsubstituted radical has been extensively investigated.[5]

The *o*-fluorine hfs constants in triphenylmethyl radicals were found to be anomalously low.[1a] These anomalous *ortho* splittings were explained on the basis of a direct interaction between fluorine orbitals and the spin density centered on the methyl carbon atom. A similar effect, but of different magnitude, is expected for *ortho*-fluorinated benzophenone anion radicals. The existence of such an effect and the fact that it does, indeed, have a different magnitude support the interpretation in terms of a direct interaction.

Experimental Section

The methods for preparations of the compounds used in the generation of the radicals are described below. All the melting points reported are uncorrected and were obtained on an electrothermal melting point apparatus. Infrared spectra were obtained on a Beckman IR-8 spectrophotometer or a Perkin-Elmer Infracord Model 137 spectrophotometer, using sodium chloride cells. A Varian A-60 spectrometer was used in determining the proton magnetic resonance spectra. Additional details of the preparations, in particular the preparation of the carbinol starting materials, can be found elsewhere.[1b]

Benzophenone. Commercially available benzophenone (mp 47–48°) manufactured by Eastman Organic Chemicals Department of Eastman Kodak Co. was used directly without further purification.

Decafluorobenzophenone. Bis(pentafluorophenyl)methanol, 9.5 g, prepared according to the directions of Barbour, *et al.*,[6] 40 g of chromium trioxide, and 200 ml of glacial acetic acid were refluxed for 15 min and then poured into a mixture of crushed ice and water. The white precipitate, collected, after filtration, was recrystallized from ethanol, mp 92° (lit. 91–92°).[5]

2,3,4,5,6-Pentafluorobenzophenone. 2,3,4,5,6-Pentafluorobenzophenone was prepared by chromium trioxide oxidation of 2,3,4,5,6-pentafluorobenzhydrol in glacial acetic acid. The benzhydrol was, in turn, prepared by refluxing for 18 hr a 1:1 molar ratio of benzaldehyde and pentafluorophenylmagnesium bromide. The 2,3,4,5,6-pentafluorobenzophenone was obtained as a low-melting, white crystalline solid, mp 33–34°, bp 85–90° (0.2 mm).

4,4′-Difluorobenzophenone. 4,4′-Difluorobenzophenone was prepared by the oxidation of bis(4-fluorophenyl)methanol with chromium trioxide in glacial acetic acid.

Bis(4-fluorophenyl)methanol. To a dry 150-ml three-necked flask equipped with a stirrer and a dropping funnel, 7.3 g (0.040 mol) of *p*-fluorobromobenzene in 50 ml of ether was added under a nitrogen atmosphere. The stirred solution was cooled to −70° with acetone–Dry Ice. *n*-Butyllithium (0.04 mol) in 16.6 ml of hexane solution was added dropwise over a period of 15 min. The mixture was stirred for 2 hr. Ethyl formate, 1.48 g (0.020 mol), in 25 ml of ether was added to the mixture, and the temperature was raised to −25°. The mixture was stirred for an additional 3 hr. The mixture was then hydrolyzed with dilute hydrochloric acid and extracted with ether. Removal of ether gave 6.8 g of crude benzhydrol whose infrared spectrum showed a strong absorption in the OH band region. The product was used for oxidation without further purification.

4,4′-Difluorobenzophenone. Crude bis(4-fluorophenyl)methanol (6.5 g) was refluxed with 30 g of chromium trioxide in 150 ml of glacial acetic acid for 20 min and then poured into a mixture of crushed ice and water. A white precipitate, collected on filtration, was recrystallized from ethanol, mp 106–107° (lit. 107.5–108°).[7] The yield was 48%, based on *p*-fluorobromobenzene. The infrared spectrum showed a strong carbonyl band, while the OH band completely disappeared.

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[1] (a) Part I has been published as a communication: S. V. Kulkarni and C. Trapp, *J. Amer. Chem. Soc.*, **91**, 191 (1969). Part II: S. V. Kulkarni and C. Trapp, *ibid.*, **92**, 4801 (1970). (b) Details of this work may be found in the thesis of S. V. K., which was submitted in partial fulfillment of the requirements for the Ph.D. degree, to the graduate school of Illinois Institute of Technology, Chicago, Ill., June 1969. (c) This work was presented in part at the Symposium on Fluorine Containing Free Radicals held during the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 8–12, 1969.

[2] Address correspondence to this author at the Department of Chemistry, University of Louisville.

[3] D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Mol. Phys.*, **5**, 407 (1962).

[4] J. K. Brown and W. G. Williams, *Trans. Faraday Soc.*, **64**, 298 (1968).

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[6] A. K. Barbour, M. W. Baxton, P. L. Coe, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 173, 808 (1961).

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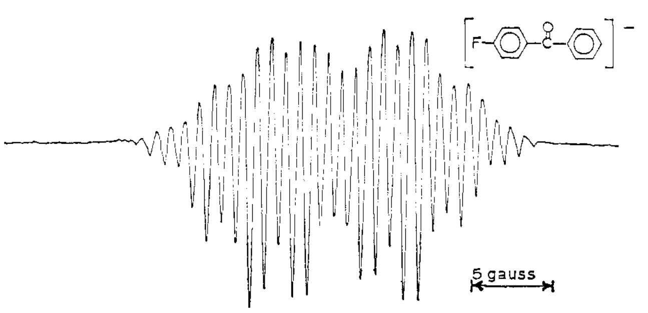

Figure 1. The esr first-derivative spectrum of electrolytically generated 4-fluorobenzophenone-F_1 anion radical in DMF solution at room temperature.

Bis(2,6-difluorophenyl)methanol. This was prepared in a manner similar to bis(4-fluorophenyl)methanol (see above), but using *m*-difluorobenzene as the starting material.

2,2′,6,6′-Tetrafluorobenzophenone. Crude bis(2,6-difluorophenyl)methanol (7 g) was refluxed with 30 g of chromium trioxide in 200 ml of glacial acetic acid. The mixture was stirred and refluxed overnight. After it was cooled to room temperature, the reaction mixture was poured into the mixture of crushed ice and water. The white precipitate obtained on filtration was recrystallized twice from ethanol. The infrared spectrum of the pure compound showed the characteristic carbonyl absorption band, while the OH band disappeared; mp 98.5–99.5°.

Preparation of Benzophenone Anion Radicals. Benzophenone and substituted benzophenone anion radicals were generated electrolytically by constant potential electrolysis in a cell placed directly in the microwave resonance cavity (intramuros). Dimethylformamide (DMF) was used as a solvent after removal of dissolved oxygen. Tetra-*n*-butylammonium perchlorate was used as a supporting electrolyte, following the considerations discussed by Maki and Geske.[8,9] Tetra-*n*-butylammonium perchlorate was prepared by precipitation from the aqueous solution of tetra-*n*-butylammonium chloride (Eastman Organic Chemicals Co.) with an equivalent amount of perchloric acid. The solubility of tetra-*n*-butylammonium perchlorate is sufficiently small at room temperature so that almost quantitative precipitation occurs. The precipitate was repeatedly washed with water, recrystallized, and dried before use.

Platinum wire was used as an anode and the sample reduction took place near the mercury surface in the flat portion of the electrolytic cell. A Varian V-4536 electrolytic flat cell was used along with a Heathkit Model IP-32 regulated power supply. The half-wave potentials for the sample reductions were obtained using an Electrochemograph Type E made by Leeds and Northrup Co., Philadelphia, Pa.

Ordinarily 10^{-3} *M* solutions of the ketones were employed in the electrolysis along with a 5×10^{-3} *M* solution of supporting electrolyte in oxygen-free DMF. The strength of the solution was adjusted by observing the line width of the esr signal. Dilute solutions gave narrower line widths but poorer signal-to-noise ratios. The solutions were diluted until further dilutions did not cause an apparent change in the line widths. The color of all the anions was found to be deep blue to violet. Nitrogen was slowly bubbled through the solutions during electrolysis.

Electron Spin Resonance Spectra. Esr spectra were obtained with the spectrometer described in part II.[1a] A Varian V-4536 electrolytic flat cell, in which the radical was generated as described above, was placed in a Varian V-4531 multipurpose cavity. The esr spectra obtained were simulated using the SESRS program described in part II.[1a]

Results

Benzophenone Anion Radical. Electrolysis of a 10^{-3} *M* solution of benzophenone in dimethylformamide (DMF) with tetra-*n*-butylammonium perchlorate as a supporting electrolyte gave a deep blue color at the mercury cathode. The splitting constants given in Table I and determined by spectrum simulation are very close to those obtained by Rieger and Fraenkel.[5]

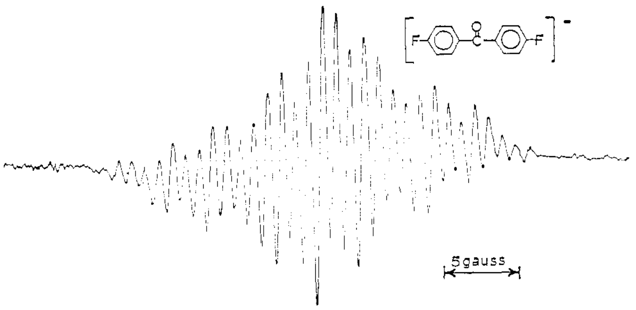

Figure 2. The esr first-derivative spectrum of electrolytically generated 4,4′-difluorobenzophenone-F_2 anion radical in DMF solution at room temperature.

4-Fluorobenzophenone–F_1 Anion Radical. The esr spectrum of the radical has not been observed previously. A large splitting of 7.29 G due to a nucleus of spin $^1/_2$ was seen in the spectrum and attributed to the *p*-fluorine atom. The second-largest splitting of 3.38 G was assigned to the one *p*-hydrogen atom. The splittings from the *o*-hydrogen atoms on both aromatic rings were found to be very close to each other in magnitude. The same was true of both sets of *meta* splittings. The possibility of obtaining small differences between the equivalent positions on the two rings was considered during the simulation. However, the best fit to the experimental spectrum was obtained when the four *o*-hydrogen atoms were treated as equivalent, and similarly for the four *m*-hydrogen atoms. We estimate that any differences between the two rings must be less than 3%. Figure 1 shows the experimental esr spectrum of this radical. The hfs constants are given in Table I.

Table I. Observed Hyperfine Splitting Constants[a] in Fluorine[b]-Substituted Benzophenone Anion Radicals in DMF

Anion radical of	a_p	a_m	a_o
Benzophenone	3.50	0.833	2.52
4-Fluorobenzophenone	$\underline{7.27}$	0.91	2.75
	3.38		
4,4′-Difluorobenzophenone	$\underline{7.42}$	0.915	2.75
2,6,2′,6′-Tetrafluorobenzophenone	3.33	0.833	$\underline{4.125}$
2,3,4,5,6-Pentafluorobenzophenone	$\underline{5.88}$	$\underline{1.14}$	$\underline{4.08}$
	3.25	0.90	2.75

[a] All the hyperfine splitting constants in gauss. [b] Fluorine hyperfine splittings are underlined.

4,4′-Difluorobenzophenone–F_2 Anion Radical. About 33 of the possible 75 hyperfine components of the spectrum could be observed (Figure 2). The hfs constants are given in Table I. The spectrum of this radical has not been reported previously.

2,2′,6,6′-Tetrafluorobenzophenone–F_4 Anion Radical. This radical has not been observed previously. The experimental spectrum is shown in Figure 3. The hfs constants are given in Table I.

2,3,4,5,6-Pentafluorobenzophenone–F_5 Anion Radical. This radical has not been studied before by esr and, in fact, is comparatively short-lived. It eventually gives a yellow-brown deposit on the mercury cathode in the electrolytic cell. The observed spectrum of the radical

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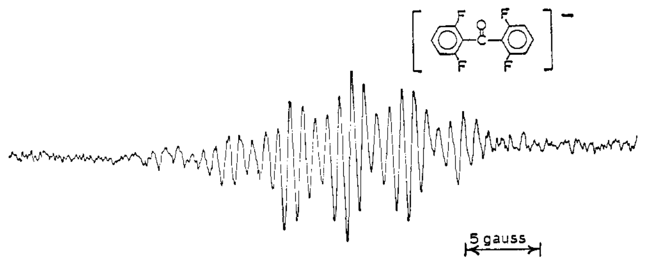

Figure 3. The esr first-derivative spectrum of electrolytically generated 2,2′,6,6′-tetrafluorobenzophenone-F_4 anion radical in DMF solution at room temperature.

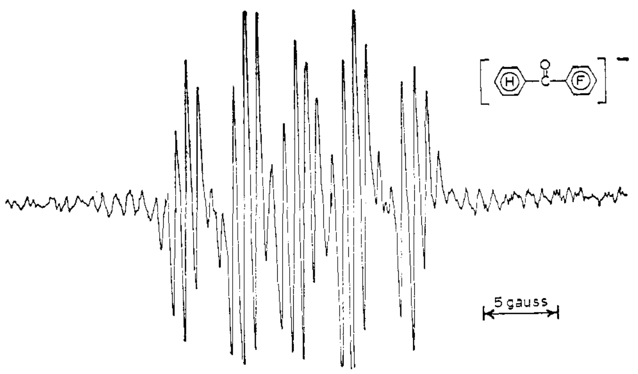

Figure 4. The esr first-derivative spectrum of electrolytically generated 2,3,4,5,6-pentafluorobenzophenone-F_5 anion radical in DMF solution at room temperature.

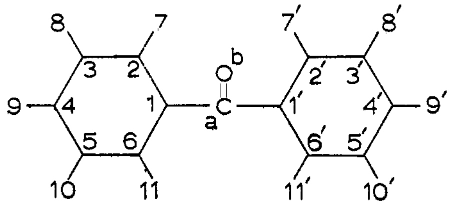

Figure 5. Numbering system for atomic positions in the benzophenone anion radicals discussed in the text.

in DMF shows five major groups of lines which are further split into groups of five lines (Figure 4). The maximum possible number of lines is 324, and there is considerable overlap of the hyperfine components. Simulation of the spectrum of this radical was somewhat more difficult than simulation of the others. The computer simulation suggested the assignment of 5.88 G for the *p*-fluorine and 3.25 for the *p*-hydrogen. One triplet splitting of 4.08 G due to two equivalent nuclei was assigned to *o*-fluorine atoms, while the triplet with splitting of 2.75 G was assigned to the two *o*-hydrogen atoms. The smaller splitting of 0.91 G was assigned to four nuclei in the *meta* position. The small difference in the *m*-fluorine and *m*-hydrogen splittings could not be resolved further because of the limitations set by the broad line widths.

Decafluorobenzophenone-F_{10} Anion Radical. Various attempts to generate this radical electrolytically under the same conditions used for the generation of the other radicals did not give reproducible results. The polarographic studies of the other radicals gave a straightforward result for the half-wave potential, indicating a one-electron transfer process. In the case of decafluorobenzophenone a complex pattern of curves was obtained when the polarogram was taken. Brown and Williams[4] were also unsuccessful in obtaining the spectra of the completely fluorinated anion radical. They could obtain a well-resolved spectrum only on photolysis of the decafluorobenzophenone in basic ethanolic solution. Their analysis showed splittings due to two sets of four equivalent nuclei of spin $^1/_2$. The triplet splitting due to the 4,4′-fluorine atoms was not observed, even though the molecular orbital calculations indicated the same order of magnitude for the spin densities centered on *o*- and *p*-carbon atoms. They concluded that the spectrum was due to 4,4′-dimethoxyoctafluorobenzophenone anion radical, which was formed due to the nucleophilic attack on the *para* positions. It was found that nucleophilic attack can occur fairly readily in the highly fluorinated system at the *ortho* and *para* positions.[10] Owing to steric considerations, the nucleophilic attack is expected to occur only at the *para* position in this radical.[4] They assigned a splitting of 4.60 G to the four equivalent *o*-fluorine atoms and 1.14 to the four *m*-fluorine atoms.

Spin Density Calculations.

Spin density distributions for this series of benzophenone anion radicals were obtained from McLachlan's approximate SCF method based on Hückel atomic orbitals.[11] The considerations involved in these calculations were discussed in part II.[1a] Rieger and Fraenkel[5] have studied in detail the molecular orbital parameters of the carbonyl group in their fitting of the data on the unsubstituted benzophenone anion radical. They found a good correlation between calculated spin densities and experimental hfs constants for a series of carbonyl anion radicals by adjusting three molecular orbital parameters, the coulomb integral parameter, h_O, for the carbonyl oxygen atom, the resonance integral parameter, k_{C-O}, and k_{C-C}, the resonance integral parameter between the carbonyl carbon atom and the ring carbon atom. The best values of the parameters arrived at by Rieger and Fraenkel were $h_O = 1.5$, $k_{C-O} = 1.6$, and $k_{C-C} = 0.9$. We have used these parameters in all our calculations.

For the fluorine-substituted benzophenone anion radicals we have used the same fluorine parameters as used on triphenylmethyl in part II[1a] and originally suggested by Eaton, *et al.*;[3] that is, $h_F = 2.5$ and $k_{C-F} = 0.619$. The results of the calculations are presented in Table II. Figure 5 gives the numbering system for atomic positions used in the calculations.

Discussion

We have shown in the previous article in this series (part II)[1a] that one-parameter equation analogous to McConnell's relationship[12] is not sufficient to describe the fluorine hfs in a series of substituted triphenylmethyl radicals. Table III gives the values of Q_{eff}^F determined for the series of fluorine-substituted benzophenone anion radicals, which is the subject of the present article. The values listed for Q_{eff}^F vary by almost a factor of 2 within this series of compounds. It seems clear that the one-parameter equation is also not sufficient in this series of radicals.

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(10) J. C. Tatlow, *Endeavour*, **22**, 89 (1963).

(11) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

(12) H. M. McConnell, *J. Chem. Phys.*, **24**, 362 (1956).

Table II. Calculated Spin Densities for Fluorinated Benzophenone Anion Radicals[a]

Compound	ρ_1	ρ_2	ρ_3	ρ_4	ρ_a	ρ_b	ρ_7	ρ_8	ρ_9
Benzophenone									
Hückel molecular orbital	0.0455	0.0764	0.006	0.0971	0.2392	0.1535			
Approximate SCF; McLachlan $\lambda = 1.2$	0.0267	0.0973	−0.0317	0.1322	0.2728	0.1471			
4-Fluorobenzophenone									
Hückel molecular orbital	0.0381 (0.0496)[b]	0.0734 (0.0773)	0.033 (0.0066)	0.0901 (0.1020)	0.2418	0.1534			0.0038
Approximate SCF; McLachlan $\lambda = 1.2$	0.0174 (0.0312)	0.0973 (0.1008)	−0.0339 (−0.0325)	0.1214 (0.1391)	0.2771	0.1471			0.0034
4,4′-Difluorobenzophenone									
Hückel molecular orbital:	0.0420	0.0763	0.0037	0.0948	0.2451	0.1535			0.0040
Approximate SCF; McLachlan $\lambda = 1.2$	0.0214	0.1011	−0.0350	0.12817	0.2821	0.1474			0.0036
2,6,2′,6′-Tetrafluorobenzophenone									
Hückel molecular orbital	0.0348	0.0739	0.0072	0.1007	0.2379	0.1471	0.0031		
Approximate SCF; McLachlan $\lambda = 1.2$	0.0167	0.0963	−0.0300	0.1381	0.2744	0.1409	0.0024		
2,3,4,5,6-Pentafluorobenzophenone									
Hückel molecular orbital	(0.0562) (0.0269)	(0.0806) 0.0700	(0.0076) 0.0030	(0.1089) 0.0829	0.2419	0.1505	0.0029	0.0001	0.0035
Approximate SCF; McLachlan $\lambda = 1.2$	(0.0387) 0.0030	(0.1050) 0.0930	(−0.0330) −0.0304	(0.1489) 0.1120	0.2791	0.1447	0.0024	−0.0014	0.0031
Decafluorobenzophenone									
Hückel molecular orbital	0.0353	0.0766	0.0045	0.0936	0.2478	0.1491	0.0031	0.0002	0.0038
Approximate SCF; McLachlan $\lambda = 1.2$	0.0119	0.1019	−0.0325	0.1276	0.2887	0.1434	0.0026	−0.0015	0.0055

[a] See Figure 5 for labeling of positions. [b] Spin densities on the corresponding positions in unsubstituted phenyl ring in parentheses.

Table III. Effective Spin Polarization Constants, Q_{eff}^{F}, and the Ratios of Fluorine and Hydrogen hfs Constants, $|a_F/a_H|$, for Fluorinated Benzophenone Anion Radicals

Anion radical of	a_F, G	a_H, G	ρ_C^{π} [a]	Q_{eff}^{F}	$\lvert a_F/a_H \rvert$	Ref
4-Fluorobenzophenone	7.27	3.50	0.147	49.4	2.08	b
4,4′-Difluorobenzophenone	7.42	3.50	0.147	50.4	2.12	b
2,3,4,5,6-Pentafluorobenzophenone	7.25 (4)	3.50	0.147	49.2	2.07	b
	4.00 (2)	2.52	0.106	37.8	1.59	b
	0.950 (3)	0.83	0.035	27.0	1.14	b
2,2′,6,6′-Tetrafluorobenzophenone	4.125	2.52	0.106	39.0	1.64	b
4,4′-Methoxyfluorobenzophenone	4.60 (2)	2.52	0.106	43.5	1.83	4
	1.14 (3)	0.83	0.035	32.5	1.37	4

[a] Determined from $a_H = Q_{CH}^{H}\rho_C^{\pi}$ with $Q_{CH}^{H} = -23.7$ G and a_H values taken from the unsubstituted benzophenone. [b] This work.

Table IV. Calculated Fluorine Splittings in Benzophenone Anion Radicals Using the Two-Parameter Equation[a]

Compound	Fluorine splittings, G		Percentage deviation
	Obsd	Calcd	
4-Fluorobenzophenone			
p-Fluorine	7.27	6.78	+7
4,4′-Difluorobenzophenone			
p-Fluorine	7.42	7.25	+4
2,3,4,5,6-pentafluorobenzophenone			
m-Fluorine	1.14	1.126	+1
p-Fluorine	5.88	6.29	−7

[a] Fluorine splittings calculated with $Q_{CF}^{F} = -85.1$ and $Q_{FC}^{F} = +1043$ G.

In the preceding article, we arrived at values of Q_{CF}^{F} and Q_{FC}^{F} which, in conjunction with eq 2 of part II, seem to fit the data on triphenylmethyl radicals. Table IV shows the result of the application of these parameters to the series of fluorine-substituted benzophenone anion radicals. Once again the deviations of the calculated and experimental values are within ±7% for the *para* and *meta* positions.

As anticipated in the case of these radicals, the observed *ortho* hfs constants were found to be smaller than those calculated on the basis of the two-parameter equation. We note, however, that the values of Δa_F for the benzophenone radicals are considerably different from what was found in the triphenylmethyl radicals. This leads us to believe that the "*ortho* effect" in both cases is, indeed, real. If the observed nonzero values of Δa_F were not due to a direct interaction mechanism as suggested, then we might find that Δa_F does not vary from one series of radicals to another. More likely we might find that a_F/a_H at *ortho* positions is invariant from one series of radicals to another. The fact that both Δa_F and a_F/a_H do vary implies that the effect is a result of a direct interaction with the "central" atoms which will have different wave functions in different types of radicals.

In conclusion, it can be said that, despite the limitations in the calculations discussed in this article and the previous article,[1a] the results of these investigations indicate that the observed fluorine hfs in aromatic radicals can probably be correlated with the two-parameter equation originally suggested by Eaton, *et al.*[3]

Ionic Interactions in Solution. I. Nuclear Magnetic Resonance Studies

R. P. Taylor[1] and I. D. Kuntz, Jr.

Contribution from Frick Chemical Laboratory, Princeton University, Princeton, New Jersey 08540. *Received December 16, 1969*

Abstract: Nmr spectra of numerous quaternary onium salts have been obtained in a variety of solvents. The magnitude of the solvent shift for a given ion in an aromatic solvent depends upon such factors as ion size and shape, solvent polarity, and the nature of the counterion. Our results are used to assess the importance of these factors in determining the extent of ion association and the nature of the associated species in solution. The experimental evidence suggests that both contact and solvent-separated species can form, with small ions in general forming more contact species.

The understanding of the nature of ionic solutions has been greatly extended through application of spectroscopic techniques. Use of absorption spectroscopy has facilitated differentiation between contact and solvent-separated ion pairs.[2] Information relating to ion pair geometries has been obtained through nmr studies of salts of transition metal complexes.[3] Recent spectroscopic and conductometric investigations have revealed that ion association in solution can be influenced by specific ion–solvent interactions which do not explicitly depend upon the dielectric constant of the medium.[4–6] A more thorough investigation of the importance of these interactions in determining the properties of ionic solutions would be desirable.

In proton nmr experiments the aromatic solvent induced shift (ASIS) experienced by polar molecules in aromatic solvents has been used to solve numerous structural problems.[7] As would be expected, the chemical shifts of ions dissolved in aromatic solvents are also strongly influenced by magnetic anisotropy effects. In this paper the ASIS experienced by a variety of cations and anions in low-dielectric aromatic solvents is examined, and the observed dependence of the ASIS on both ion–ion and ion–solvent interactions is discussed. These interactions are shown to depend on the size, shape, and charge density of the molecules involved.

Experimental Section

Nmr Spectra. Samples were run on a Varian A60-A spectrometer equipped with a variable temperature probe. Solvents, either reagent or spectroscopic grade, were obtained from the usual commercial sources, dried over molecular sieves (Matheson Coleman and Bell "Linde" Type 4A), and used without further purification.[8] Chemical shifts, recorded in hertz, were measured relative to internal tetramethylsilane (TMS, 1% v/v) by the usual side-band techniques and were in general reproducible to ±1 Hz. Downfield frequencies are shown as negative. Chemical shifts are taken as the centers of gravity of multiplets. Ion association had no observable effect on the ^{31}P–H coupling constant (~13 to 13.5 Hz).[9] All chemical shifts refer to α-methyl resonances unless otherwise specified. The estimated uncertainty in the quadrupole broadened resonance of the CH$_3$B group was ±2 Hz. Temperatures were measured using the Varian-supplied methanol or ethylene glycol samples. Most experiments were performed at probe temperature (40 ± 2°).

Preparation of Compounds. Quaternary onium salts were either purchased commercially or synthesized by standard methods.[10–12] When necessary they were recrystallized from suitable solvents.[10–12] Tetraalkyl- and tetraarylboron compounds were synthesized following Damico's general procedures.[13] Many of the tetraalkylboron compounds are air sensitive and subsequently were stored under nitrogen until they were used. New compounds and those whose melting points disagreed with literature values were checked by elemental analysis. Satisfactory results were obtained in all cases (Appendix).

Results

1. Cations. The α-methyl resonance frequency of methyl tributylammonium picrate is strongly solvent dependent (Table I). We ascribe these effects to cation solvation because the large differences in solvent shifts are not reduced at lower salt concentrations, indicating that ion association cannot be responsible. Reaction field[14] effects are apparently unimportant as there is

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