Electron Spin Resonance of Trifluoromethylnitrobenzene Radical Anions. Hindered Rotation of the *o*-Trifluoromethyl Group[1,2]

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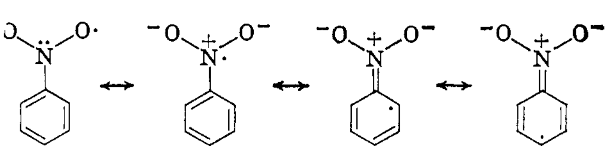
Abstract: Electron spin resonance spectra of *o*-, *m*-, and *p*-trifluoromethylnitrobenzene radical anions have been obtained in acetonitrile. The trifluoromethyl group experiences hindrance to free rotation in *o*-trifluoromethylnitrobenzene anion radical, resulting in the complete absence of $M_N = \pm 1/2$ lines in the trifluoromethyl multiplet. The same result is obtained in 4-amino- and 4-methoxy-2-trifluoromethylnitrobenzene anion radicals. 4-Hydroxy-2-trifluoromethylnitrobenzene gives a spectrum showing marked line-width alternation. The data obtained for *o*-trifluoromethylnitrobenzene radical anions is consistent with p–π interaction between p orbitals of fluorine and the π-electron system.

The one-electron reduction of nitrobenzene and substituted nitrobenzenes is known to produce stable nitrobenzene radical anions. A large number of substituted nitrobenzene radical anions have been studied by electron spin resonance in a variety of solvents.[3–12] The ease of generating the nitrobenzene radical anion by chemical or electrolytic means and the ease with which the complete hyperfine spectrum can be resolved and analyzed make this radical anion particularly attractive for studies of substituent effects. In this paper the electron spin resonance of trifluoromethylnitrobenzene radical anions is described.

Nitrobenzene free radical anion produced by electrolytic reduction in acetonitrile gives a spectrum of 54 lines. The coupling constants are $A_N = 10.32$, $A_o^H = 3.39$, $A_m^H = 1.09$, $A_p^H = 3.97$,[5a] and $A_O^{17} = 8.86$ gauss.[5c]



In ethers or other aprotic solvents similar values are obtained.[4d,5e,7c,9b] In protic solvents the nitrogen coupling constant is larger, *e.g.*, $A_N = 13.87$ in water.[7a] The increase in the nitrogen coupling constant in protic solvents is attributed to hydrogen-bonding solvation of the nitro group.[7c,9a]

The spectra of *meta*- and *para*-substituted nitrobenzene radical anions show that the nitrogen coupling constant decreases with electron-withdrawing groups and increases with electron-donating groups.[5c,6] Of further significance is the observation that the substituents themselves contribute to the hyperfine splitting. Sizable splitting from the hydrogens in the methyl, amino, methoxy, and aldehydic groups, nitrogen in the amino and cyano groups, and phosphorus in phosphate groups is resolved in the spectra of the correspondingly *para*-substituted nitrobenzene radical anions.[5,6,9b] Apparently in general spin is readily transferred to nuclei bonded in a position β to the orbital containing the unpaired electron.

The esr spectra of *ortho*-substituted nitrobenzene radical anions show the effect of steric hindrance. Bulky groups in the *ortho* position increase the nitrogen coupling constant.[5d] This is attributed to an increased localization of the unpaired electron on the nitro group as this group is twisted out of the plane of the aromatic ring.

The esr spectra of polynitrobenzene radical anions have been of interest for some time. The spectrum of *m*- and *p*-dinitrobenzene radical anion is very solvent dependent. In ether only one large nitrogen coupling constant is observed (*e.g.*, for *m*-dinitrobenzene, $A_N = 9.0$ and 0.29 gauss in 1,2-dimethoxyethane)[4e] but in polar aprotic solvents both nitro groups have the same coupling constant (*e.g.*, for *m*-dinitrobenzene, $A_N = 4.68$ gauss in acetonitrile.)[5b] These observations are

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(2) This work was supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society. Grateful acknowledgment to the donors of this fund is hereby made.

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(9) (a) J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2832 (1962); (b) P. H. Rieger and G. K. Fraenkel, *ibid.*, **39**, 609 (1963); (c) J. H. Freed and G. K. Fraenkel, *ibid.*, **37**, 1156 (1962); (d) J. H. Freed, P. H. Rieger, and G. K. Fraenkel, *ibid.*, **37**, 1881 (1962); (e) I. Bernal and G. K. Fraenkel, *J. Am. Chem. Soc.*, **86**, 1671 (1964); (f) M. Kaplan, J. R. Bolton, and G. K. Fraenkel, *J. Chem. Phys.*, 42, 955 (1965); (g) R. D. Allendoerfer and P. H. Rieger, *ibid.*, **46**, 3410 (1967).

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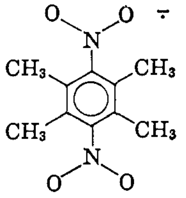
interpreted in terms of ion-pair formation. In ether the metal ion is thought to be closely associated with one nitro group only but in acetonitrile the radical is considered to be essentially a free ion. However, recently a new interpretation of these results has been presented.[6c,13] It has been found that spectra of *m*- and *p*-dinitrobenzene radical anions in solvent mixtures of intermediate polarity, *e.g.*, dimethylformamide, ethanol or methanol, dioxane, show broad lines when $M_N = \pm 1$ and sharp lines when $M_N = 0, \pm 2$. (M_N is the total *z* component of the nitrogen nuclear spin angular momentum.) Such spectra are said to exhibit line-width alternation.[9c-e,g,14] Line-width alternation is observed when the magnitude of certain coupling constants changes rapidly as a function of time. In the case of the dinitrobenzene radical anions the nitrogen coupling of each nitro group appears to alternate rapidly between two values. This may be the result of rapid oscillation of the metal ion between the two nitro groups,[13,15] or rapid formation of short-lived solvent complexes.[9d,g]

Time-dependent nitrogen coupling constants are also observed in highly hindered dinitrobenzene radical anions, *e.g.*, dinitrodurene (I), dinitromesitylene, and trinitromesitylene.[9c,e,g] The spectrum obtained from dinitrodurene anion radical shows five groups of lines alternatingly sharp and broad. The rotational motion of the crowded methyl and nitro groups leads to a difference in planarity of the nitro groups with respect to the phenyl ring. The more twisted nitro group has a larger nitrogen coupling constant than the less twisted group. If the relative positions of the nitro groups are fixed or exist in a given conformation much longer than ~10^{-5} sec, the spectrum should show two different nitrogen coupling constants. If the nitro groups rotate extremely rapidly such that the lifetime of any one conformation is much less than ~ 10^{-7} sec, an average coupling to two equivalent nitrogen nuclei should be observed. If the nitro groups rotate at an intermediate rate such that the lifetime of any one conformation is approximately 10^{-6} sec, lines due to $M_N = \pm 1$ will be broadened while lines due to $M_N = 0, \pm 2$ will remain sharp (see diagram on p 341 of ref 14).[16]



I

Results and Discussion

Stock and Suzuki[17] first showed that sizable fluorine splitting is observed in trifluoromethyl-substituted radical anions. Thus in trifluoromethylbenzosemiquinone the splitting due to three equivalent fluorine nuclei ($I = {}^1/_2$) is 2.66 gauss. In connection with our earlier studies of substituent effects on the rate of electron-transfer reactions of carbanions with nitrobenzene derivatives[8,18] we obtained the esr spectrum of *m*-trifluoromethylnitrobenzene radical anion in *t*-butyl alcohol. We found the spectrum of *m*-trifluoromethylnitrobenzene radical anion in this solvent to be almost superimposable with the spectrum of *m*-nitrotoluene radical anion aside from a slightly smaller nitrogen coupling constant in the case of the trifluoro derivative. Further studies are reported here on the comparison of the esr spectra of trifluoromethylnitrobenzene radical anions with the corresponding nitrotoluenes.

Since this work was initiated a number of perfluorinated stable free radicals have been described. Bis(trifluoromethyl) nitroxide[19] and a number of related derivatives[20] appear to be very stable free radicals. Hexakis(trifluoromethyl)benzene radical anion has also been prepared by alkali metal reduction in tetrahydrofuran.[21]

***m*- and *p*-Trifluoromethylnitrobenzene.** Under low resolution the spectra obtained from *m*-trifluoromethylnitrobenzene and *m*-nitrotoluene are similar. As in the case of *m*-nitrotoluene radical anion where the splitting due to the *m*-hydrogen is essentially equivalent to the *m*-methyl hydrogens, the splitting due to the *m*-hydrogen of *m*-trifluoromethylnitrobenzene is also approximately equivalent to the fluorine splitting in the *m*-trifluoromethyl group. Thus both radicals show characteristic quintet groups of lines in the wings of the spectrum under low resolution. High-resolution spectra show that the fluorine coupling is somewhat larger than the *m*-hydrogen coupling. Approximately 113 lines (out of the 192 possible) have been resolved. No evidence for line-width alternation can be found. The complexity of the spectrum and the large number of unresolved lines make small line-broadening effects difficult to recognize. Line widths vary between 0.05 and 0.1 gauss, the latter occurring when neighboring lines are unresolvable.[22] The nitrogen coupling constant in *m*-trifluoromethylnitrobenzene radical anion is smaller than in nitrobenzene itself in accordance with the overall electron-withdrawing nature of the trifluoromethyl substituent. The coupling constants are assigned by analogy to previous studies of substituted nitrobenzene radical anions[4,5] (Table I).

The spectrum of *p*-trifluoromethylnitrobenzene radical[22] anion shows extraordinarily broad lines in dry acetonitrile (line width ~0.4 gauss). Attempts to obtain spectra with narrower lines by dilution or extended degassing of solutions were not successful. The spectrum can be fitted to the coupling constants listed in Table I. The coupling constants obtained for the same radical in wet acetonitrile substantiate the assignment given. In the presence of water the nitrogen coupling

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[13] (a) M. J. Blandamer, T. E. Gough, J. M. Gross, and M. C. R. Symons, *J. Chem. Soc.*, 536 (1964); (b) M. J. Blandamer, J. M. Gross, and M. C. R. Symons, *Nature*, **205**, 591 (1965); J. M. Gross and M. C. R. Symons, *Mol. Phys.*, **9**, 287 (1965).

[14] J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 326 (1963); A. Carrington, *Mol. Phys.*, **5**, 425 (1962).

[15] Rapid oscillation of a metal ion between two positions in the pyracene radical anion ion pair leads to line-width alternation: E. De Boer and E. L. Mackor, *J. Am. Chem. Soc.*, **86**, 1513 (1964).

[16] Other examples of line-width alternation can be found in ref 14.

[17] L. M. Stock and J. Suzuki, *J. Am. Chem. Soc.*, **87**, 3909 (1965); *Proc. Chem. Soc.*, 212 (1962).

[18] G. A. Russell, E. G. Janzen, A. G. Bemis, E. J. Geels, A. J. Moye, S. Mak, and E. T. Strom, "Selective Oxidation Processes," Advances in Chemistry Series, No. 51, American Chemical Society, Washington, D. C., 1965, p 112.

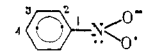
[19] (a) W. D. Blackley and R. R. Reinhard, *J. Am. Chem. Soc.*, **87**, 802 (1965); (b) P. J. Sheidler and J. R. Bolton, *ibid.*, **88**, 371 (1966).

[20] (a) W. D. Blackley, *ibid.*, **88**, 480 (1966); (b) E. T. Strom and A. L. Bluhm, *Chem. Commun.*, 115 (1966).

[21] (a) M. T. Jones, *J. Chem. Phys.*, 42, 4054 (1965); J. C. Danner and A. H. Maki, *J. Am. Chem. Soc.*, **88**, 4297 (1966).

[22] Because of referees' recommendations these spectra are not given in this paper.

Table I. Coupling Constants for Trifluoromethylnitrobenzene Anion Radicals[a]

	A_N	A_2^H	A_3^H	A_4^H	A_5^H	A_6^H
3-CF_3	8.84	3.01 or 3.21	1.2[b]	4.05	1.00	3.01 or 3.21
4-CF_3	8.0	3.20	0.92	8.0[b]	0.92	3.20
~2% H_2O	9.0	3.22	1.01	7.35[b]	1.01	3.22
2-CF_3	8.32	8.5[b]	0.9 or 1.2	3.9	1.2 or 0.9	3.0
~2% H_2O	8.62	8.3[b]	0.9 or 1.3	4.1	0.9 or 1.3	3.1
2-CF_3-4-CH_3O	9.2	9.29[b]	1.10	0.31[c]	1.10	3.00
2-CF_3-4-NH_2	10.15	9.08[b]	1.02	1.02[d] 1.02[e]	1.02	3.06
2-CF_3-4-O^-	12.1	8.38[b]	0.32 or 1.06		0.32 or 1.06	2.68
3-CF_3-4-CH_3O	10.9	4.3	1.43[b]	0.32[c]	1.43	4.3

[a] In gauss in acetonitrile at ambient temperatures. [b] Quartet splitting due to fluorine in trifluoromethyl group. [c] Quartet splitting due to methoxy hydrogens. [d] Triplet splitting due to amino nitrogen. [e] Triplet splitting due to amino hydrogens. The following coupling constants have been obtained by Professor M. T. Jones for 4-trifluoromethylnitrobenzene: $A_N = A_F = 8.34$, $A_o^H = 3.29$, $A_m^H = 0.90$ gauss (private communication), and by J. W. Rogers and W. H. Watson for 2-trifluoromethylnitrobenzene: $A_N = 8.33$, $A_F = 8.51$, $A_o^H = 3.20$, $A_m^H = 1.23$, 0.87, $A_p^H = 3.90$ gauss, and for 4-hydroxy-2-trifluoromethylnitrobenzene: $A_N = 12.62$, $A_F = 8.63$, $A_o^H = 2.68$, $A_m^H = 1.09$ and 0.38 gauss (private communication from Professor Watson).

increases by approximately one gauss while none of the other coupling constants change significantly. Resolution of the spectrum in wet acetonitrile is excellent.[22] Much narrower lines are obtained (line width ~0.1 gauss).[23] The nitrogen coupling constant is smaller in *p*-trifluoromethylnitrobenzene radical anion than in the *meta* isomer in agreement with the greater over-all electron-withdrawing nature of the trifluoromethyl group when in the *para* position.

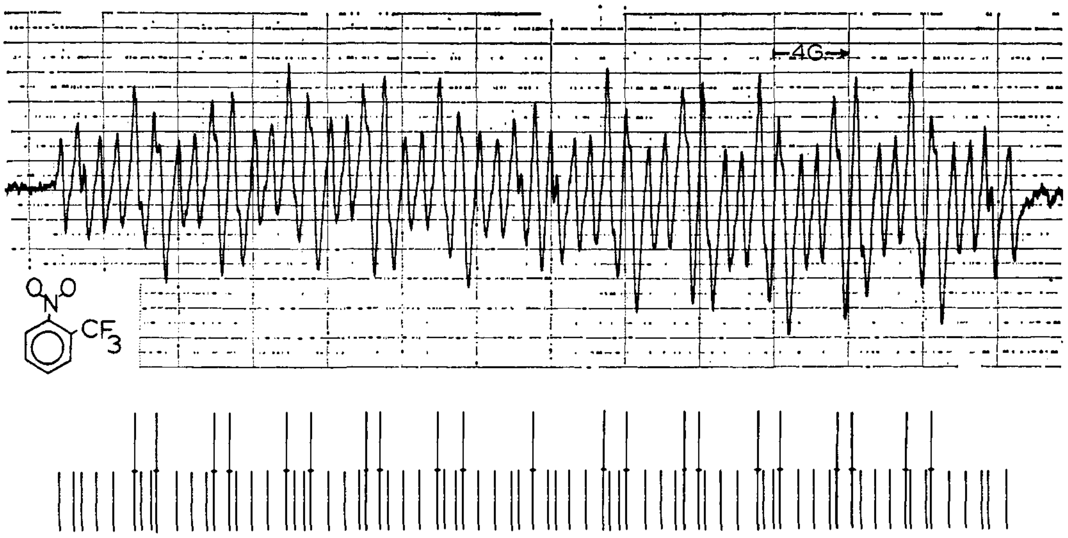


Figure 1. Esr spectrum of *o*-trifluoromethylnitrobenzene anion radical in acetonitrile.

o-**Trifluoromethylnitrobenzenes.** The spectrum of *o*-trifluoromethylnitrobenzene is shown in Figure 1. This spectrum is most unusual since out of the 192 anticipated lines for *o*-trifluoromethylnitrobenzene anion radical only approximately 74 are observed under good resolution. The almost uniform intensity of all the peaks is not in agreement with the predicted 1:3:3:1 intensity sequence expected from coupling to three equivalent fluorine nuclei in the trifluoromethyl group. Moreover if extensive coincidental overlap were present a much larger variation in intensity of peaks should be observed. The addition of small amounts of water leads to sharpening of all the lines. A small increase in total line width is observed with the addition of small amounts of water (~0.3 gauss) but the total line width decreases again with larger amounts of water.

The stick diagram in Figure 1 was constructed from a nitrogen triplet of 8.32 gauss and doublet splitting of 25.5, 3.9, 3.0, 1.2, and 0.9 gauss, respectively. The large doublet splitting is due to three times the trifluoromethyl fluorine coupling. The analysis of this spectrum can be best understood after a discussion of the spectra obtained from the following *para*-substituted *o*-trifluoromethylnitrobenzene radical anions.

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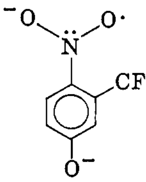
[23] The addition of 2% water to acetonitrile increases the nitrogen coupling in nitrobenzene radical anion by 1.5 gauss.[5e] The rate of electron transfer between nitrobenzene and nitrobenzene radical anion is found to diminish with addition of water: T. Layloff, T. Miller, R. N. Adams, H. Fah, A. Horsfield, and W. Proctor, *Nature*, 205, 382 (1965). Rapid electron transfer might account for some of the broadening in *p*-trifluoromethylnitrobenzene radical anion in dry acetonitrile.

4-Hydroxy-2-trifluoromethylnitrobenzene is reduced to an unstable radical in acetonitrile which gives a spectrum consisting of six broad lines at low resolution (high modulation amplitude). Under better resolution (low modulation amplitude) only five groups of sharp lines are obtained. The low-field one-sixth of the spectrum at very low modulation amplitude is shown in Figure 2. The eight sharp lines consist of three doublets. A neighboring group of four broad lines can be seen with approximately the same spacing as in the corresponding doublet of doublets in the group of sharp lines. The intensity of these groups of sharp and broad lines is very dependent on modulation amplitude. The sequence of sharp and broad groups of lines observed in the spectrum of 4-hydroxy-2-trifluoromethylnitrobenzene and the marked line width and intensity dependence on the modulation amplitude is typical of free radicals having time-dependent coupling constants.[9c-e,14]

The radical obtained by the reduction of 4-hydroxy-2-trifluoromethylnitrobenzene is probably 4-oxy-2-trifluoromethylnitrobenzene dianion radical.



The three doublets (sharp lines in Figure 2) measuring 2.68, 1.06, and 0.32 gauss are reasonable splittings for the three ring hydrogens of this radical.[24]

The sequence of sharp and broad lines observed for this radical is consistent only with a *time-dependent coupling with fluorine* and not with nitrogen. Interaction of the unpaired electron with three equivalent fluorine nuclei gives four lines with total spin $-{}^3/_2$, $-{}^1/_2$, $+{}^1/_2$, and $+{}^3/_2$. Quartets of lines due to three equivalent fluorine nuclei are in fact observed for *m*- and *p*-trifluoronitrobenzene anion radical. In this case the trifluoromethyl group is rotating freely. However, if the trifluoromethyl group is held in some conformation longer than 10^{-5} sec such that one fluorine coupling constant is different from the other two (these in turn being equal), six lines should be expected.[25] The intensity sequence depends on whether the unique coupling is larger or smaller than the two which are equal: for $A_1^F > A_2^F = A_3^F$, the intensity sequence is 1:2:1:1:2:1; for $A_1^F < A_2^F = A_3^F$, 1:1:2:2:1:1. Three cases arise for each of these situations (I, II, III and IV, V, VI, Figure 3) depending on the identification of the fluorine nucleus with a particular coupling constant. The sequences shown in Figure 3 can be generated by rotating the trifluoromethyl group through three 120° increments. These cases are not experimentally distinguishable in the event of a fixed conformation for the trifluoromethyl group. However, if the trifluoromethyl group experiences hindered rotation such that the lifetime of any conformation is between the limits of slow and fast rotation, 10^{-5}–10^{-7} sec, all lines which have different spin labels in the sequence I, II, and II or IV, V, and VI will be broadened and only lines which have identically the same spin label in every step of this sequence will remain sharp. In the most general case all three fluorine atoms could be different. Then eight lines would be expected if the trifluoromethyl group is fixed. By the same arguments only two lines would be sharp for hindered rotation of the trifluoromethyl group. All the rest of the lines would be broadened (VII–IX).

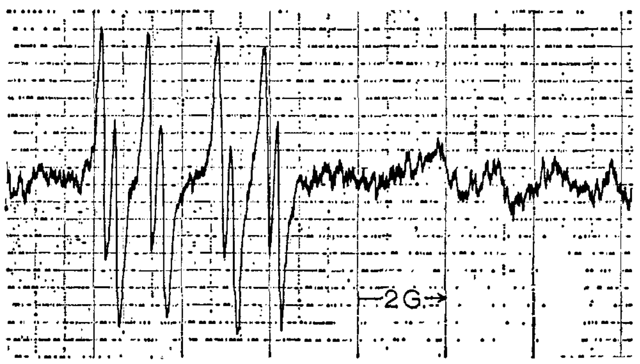
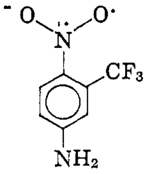
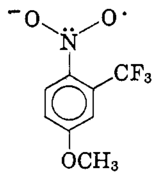


Figure 2. Low-field one-sixth of the esr spectrum of 4-oxy-2-trifluoromethylnitrobenzene dianion radical at very low (100-kcps) modulation amplitude and slow scan rate.

The sharp lines in the spectrum obtained from 4-hydroxy-2-trifluoromethylnitrobenzene are due only to the outermost ($\pm{}^3/_2$) lines of the trifluoromethyl quartet. The nitrogen triplet thus generates a total of six groups of sharp lines (two groups overlap in the center). The remaining lines of the trifluoromethyl quartet are present as broad peaks (Figure 4). The fluorine coupling constant is obtained by measuring one-third of the distance between the outermost lines of the trifluoromethyl quartet (Table I). These values agree well with measurements made from the broad peaks of the same multiplet.

In order to further substantiate our interpretation of these spectra the radical anions of 4-amino- and 4-methoxy-2-trifluoromethylnitrobenzene were investigated.





Reduction of 4-amino-2-trifluoromethylnitrobenzene radical anion gives a very stable radical with the spectrum shown in Figure 5. Again six groups of fairly sharp lines are obtained with overlap in the center as in the spectrum from 4-hydroxy-2-trifluoromethylnitrobenzene. Each group of ten lines is well fitted to reasonable coupling constants for ring hydrogens, amino nitrogen, and amino hydrogens used by previous workers for 4-aminonitrobenzene radical anion[5c] (Table I). As expected not complete coincidental overlap of these lines occurs, as shown by higher resolution of the ten-line multiplet (insert, Figure 5). The six groups of ten lines must be derived from the $\pm{}^3/_2$ lines of the trifluoromethyl quartet. No evidence for other lines can be obtained.

4-Methoxy-2-trifluoromethylnitrobenzene reduces to an unstable radical which gives the spectrum in Figure 6.

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(24) Nitrophenolate dianion radicals are found to have unusually small *m*-hydrogen coupling constants: $A_N = 12.41$, $A_o^H = 3.69$, $A_p^H = 3.69$, $A_m^H = A_O^H = 0.54$, for *o*-nitrophenolate dianion radical.[12]

(25) An example of this type of restricted rotation has been found for 1-methylanthrasemiquinone. The esr spectrum is consistent with two different coupling constants for the three methyl hydrogens: R. M. Elofson, K. F. Shulz, B. E. Galbraith and R. Newton, *Can. J. Chem.*, 43, 1553 (1965).

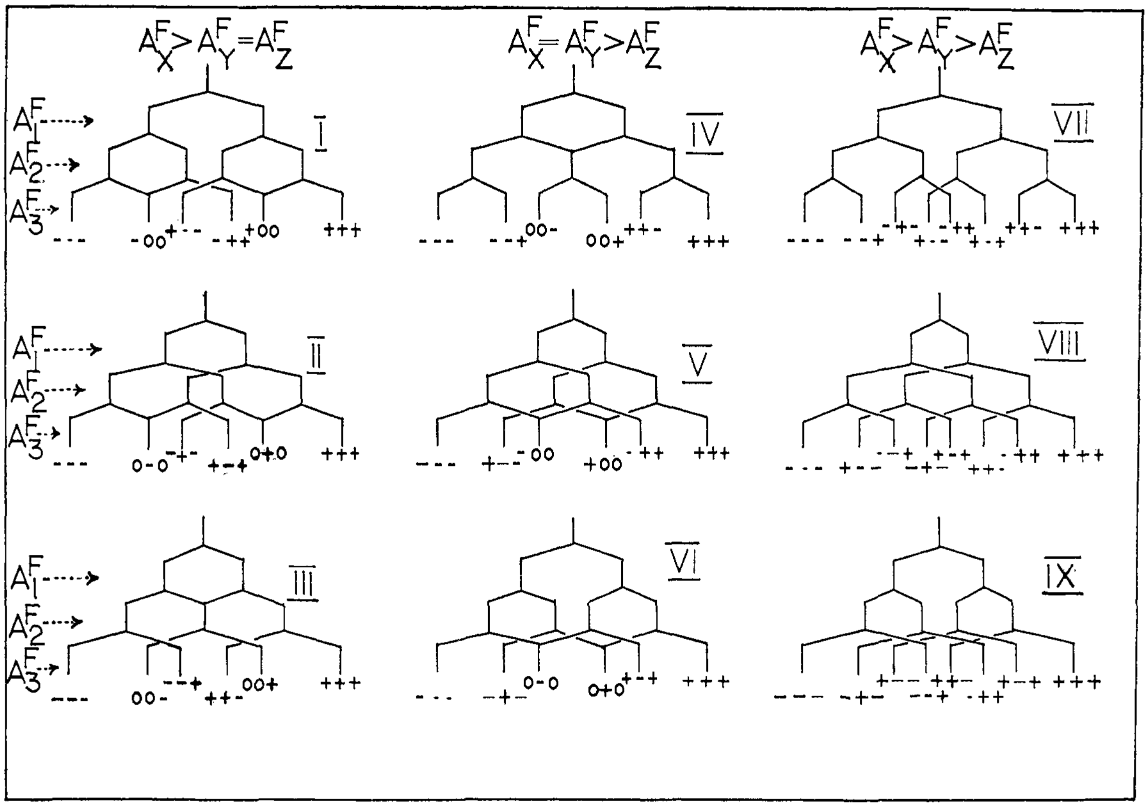


Figure 3. Esr line spectrum predicted for fluorine splitting in a rotating trifluoromethyl group. The spin labels (*e.g.*, − + −) are the spin states of 1-F, 2-F, and 3-F where − and + designate $-{}^1/_2$ and $+{}^1/_2$, respectively. Two lines in each of I–VI are doubly degenerate. The spin label is given as the algebraic sum of the spin labels of the superimposed lines, *e.g.*, second line in I is (− − +) + (− + −) = −00.

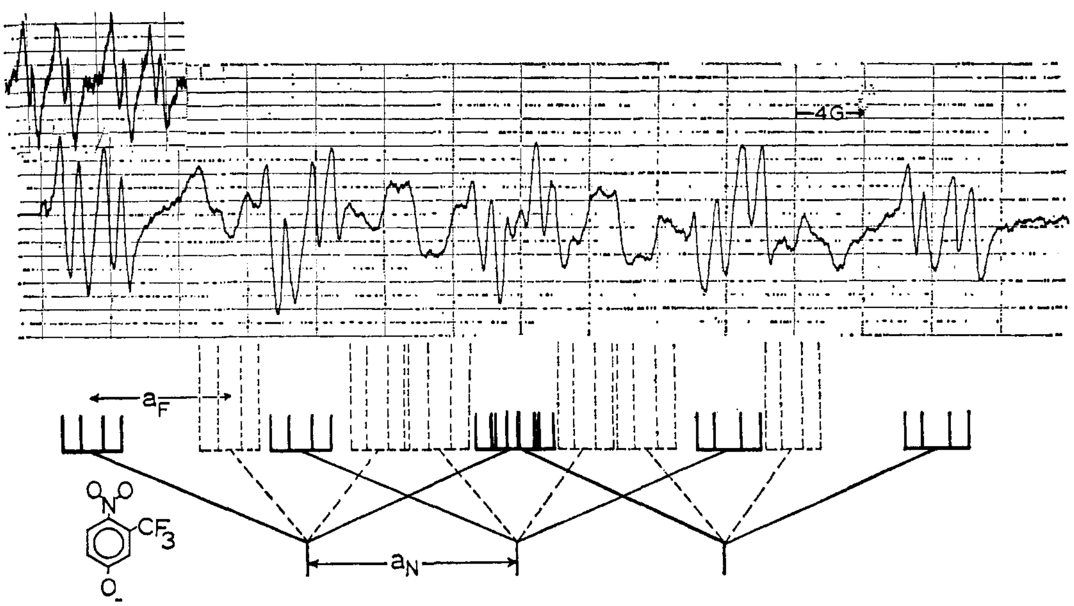


Figure 4. Esr spectrum of 4-oxy-2-trifluoromethylnitrobenzene radical dianion at low (100-kcps) modulation amplitude. Inserts shows the initial quartet resolved into eight lines under conditions of lower modulation amplitude and slower scan rate.

Six well-resolved groups of 18 lines are obtained. The 18-line multiplet is well fitted to values used by previous authors for ring and methoxy hydrogens in 4-methoxynitrobenzene radical anion[5c] (Table I). Clearly the groups of sharp lines are due to the $\pm{}^3/_2$ lines of the trifluoromethyl multiplet. This radical was found to be very unstable, a new radical with narrower total line width dominating the spectrum after nominal reduction periods. The additional broad lines in Figure 6 are probably due to this species. Thus both in 4-amino- and 4-methoxy-2-trifluoronitrobenzene it appears that no trace of the trifluoromethyl lines other than the outermost ($\pm{}^3/_2$) lines can be detected in the spectrum of these radicals.

It is of interest to note that 4-methoxy-3-trifluoromethylnitrobenzene radical anion gave a well-resolved

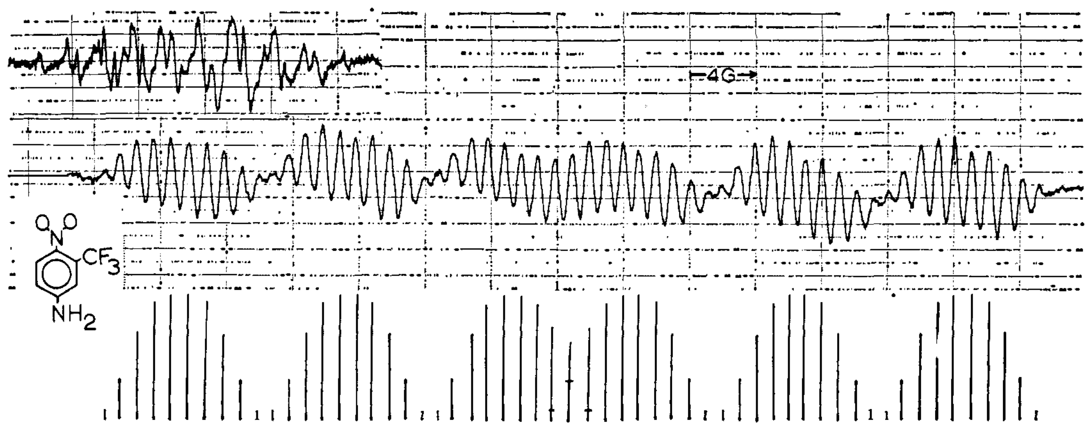


Figure 5. Esr spectrum of 4-amino-2-trifluoromethylnitrobenzene radical anion in acetonitrile. Insert is high resolution of the first branch at slower scan.

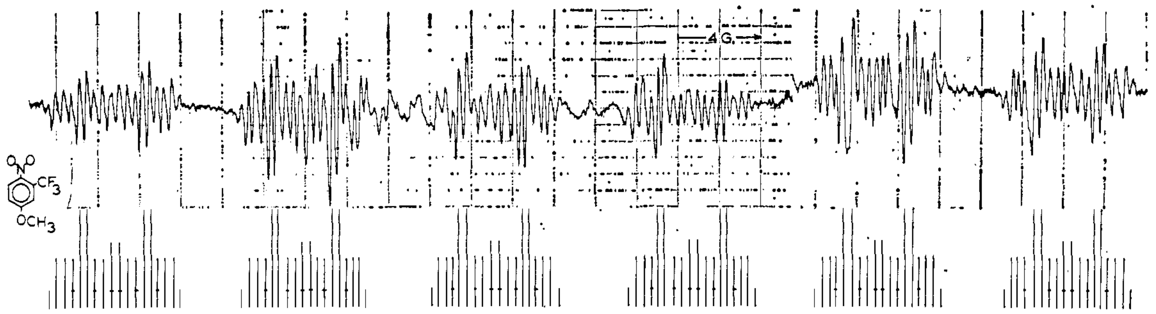


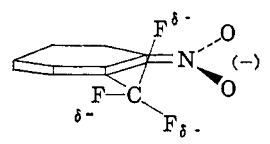
Figure 6. Esr spectrum of 4-methoxy-2-trifluoromethylnitrobenzene radical anion in acetonitrile. Because of the poor stability of this radical and the formation of a new radical during extended reduction periods the spectrum shown is made up of two recordings. Peak intensities for the six major groups of lines cannot strictly be compared.

spectrum with no evidence for line broadening. Coupling constants for this radical were readily obtained by inspection (Table I). Apparently the free rotation of the trifluoromethyl group is not hindered by neighboring groups like methoxy.

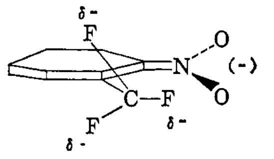
Mechanism for Fluorine Line Broadening in *o*-Trifluoromethylnitrobenzene Radical Anions. It is clear that the trifluoromethyl group experiences hindrance to free rotation in *o*-trifluoromethylnitrobenzene radical anion. Three not entirely unrelated mechanisms for restricted rotational freedom can be considered: (1) steric hindrance, (2) charge–dipole interaction, and (3) p–π orbital overlap.

Steric interaction in the usual sense between the nitro and trifluoromethyl groups does not appear to be the main reason for the observed hindered rotation since the nitrogen coupling is not increased markedly in the *ortho* isomer. The nitrogen coupling goes from 8 gauss in *p*-trifluoromethylnitrobenzene radical anion to 8.32 gauss in the *ortho* isomer. Nitrogen coupling in the nitrotoluenes increases from 10.8 in *p*-nitrotoluene to 11.0 in the *ortho* isomer. Moreover, in previous cases of line broadening caused by steric interaction with the nitro group, the nitrogen lines are broadened and not the hydrogen lines of the *ortho* alkyl group. In the *o*-trifluoromethylnitrobenzenes there is no evidence for nitrogen line broadening.

A charge–dipole interaction can be considered as the cause for hindered rotation of the trifluoromethyl group. The partially negatively charged oxygen atoms of the nitro group could interact with the negatively polarized fluorine atoms such that conformation II is more stable than III.



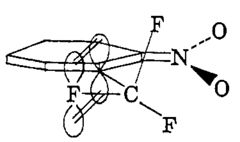
II



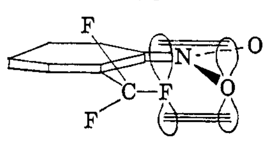
III

Hindered rotation due to charge–dipole repulsion is thus visualized. Since the carbon–fluorine bond in trifluoromethyl groups located in direct conjugation with a negatively charged site is expected to be highly negatively polarized (either by inductive[26] or hyperconjugative effects[27]) this mechanism for hindered rotation seems quite reasonable.

However one could argue that III is the preferred conformation because of the possibility of p–π bonding between the p orbitals on fluorine and oxygen.[28] Recent



II



III

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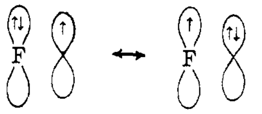
[26] A. Streitwieser, Jr., and D. Holtz, *J. Am. Chem. Soc.*, **89**, 692 (1967); A. Streitwieser, Jr., A. P. Marchand, and A. H. Pudjaatmaka, *ibid.*, **89**, 693 (1967).

[27] D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, p 68; S. Andreades, *J. Am. Chem. Soc.*, **86**, 2003 (1964).

[28] It is most reasonable to consider p orbital overlap between

work on perfluoro radicals has shown that fluorine p orbital overlap with π-electron systems is significant. Thus fluorine coupling constants in bis(trifluoromethyl) nitroxide[19b] and hexakis(trifluoromethyl)benzene radical anion[21b] are found to be temperature dependent. These results indicate that preferred conformations exist which enhance fluorine p-orbital overlap with the π-electron system. Strom has suggested that the dihedral angle for maximum fluorine splitting may be 90°.[20b] However, none of these studies prove that the preferred conformations are *stabilized* by fluorine p-orbital overlap with the π-electron system. In the *ortho* trifluoromethylnitrobenzenes one must invoke a stabilization due to fluorine p–π orbital interaction if conformation III is to be more stable than II.

Both mechanisms for hindered rotation predict an enhanced fluorine coupling. In conformation II spin transfer from the p orbital on the contiguous carbon atom to the fluorine p orbital could take place. Similarly in III spin could transfer from oxygen to fluorine.

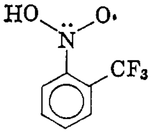


The fluorine coupling constant in fact is found to be larger in the *ortho* isomer (8.5 gauss) than in the *para* isomer (7.30 gauss). This is in direct contrast to the methyl hydrogen splitting in *o*- and *p*-nitrotoluene (3.10 and 3.98 gauss, respectively).

The effect of the addition of water is interesting. Normally the addition of water to a solution of a nitrobenzene radical anion has a large effect on the nitrogen coupling constant.[7] The nitrogen coupling in *p*-trifluoromethylnitrobenzene radical anion for example increases by 1 gauss upon addition of a small amount of water. With bulky *ortho* substituents adding water has an even larger effect.[7c] However, in a chelated nitrobenzene radical anion such as *o*-nitrobenzoic acid the addition of water has no effect on the nitrogen coupling constant.[7c] The change in nitrogen coupling constant in *o*-trifluoromethylnitrobenzene radical anion upon addition of water is very small (~0.3 gauss). This result seems surprising but indicates that a certain amount of chelation between the trifluoromethyl group and the nitro group exists.

The small change in fluorine coupling constant upon the addition of water shows that interaction of the fluorine atoms with solvent molecules has a negligible over-all effect on the rotational freedom of the trifluoromethyl group and hence the spin distribution in the radical. We have also obtained the spectrum of *o*-trifluoromethylnitrobenzene radical anion in tetrahydrofuran using lithium or sodium as a reducing agent.[29] Well-resolved spectra due to one radical species have been obtained. The spectra are obviously the same "broadened" spectra as obtained in acetonitrile. With sodium, quartet splitting due to the metal ion hyperfine ($I = {}^3/_2$; $A_{\mathrm{Na}} = 0.29$ gauss) is resolved. Thus the sodium contact ion pair also shows hindered rotation of the trifluoromethyl group.

It would appear that a choice between the two mechanisms for fluorine line broadening could be made if the spectrum for a *neutral* *o*-trifluoronitrobenzene radical could be obtained. Charge–dipole interactions should then be less important and reduced to dipole–dipole interactions wheras p–π orbital interactions which depend only on the spin density should not be affected. We have obtained the spectrum of such a radical by the photolysis of *o*-trifluoromethylnitrobenzene in tetrahydrofuran.[29,30]



This spectrum shows the usual features for these types of radicals. No evidence for fluorine line-width broadening has been obtained. Tentatively, we must conclude that the charge–dipole interaction mechanism is the most likely one for fluorine line-width alternation for *o*-trifluoromethylnitrobenzene radical anions. Further studies are in progress.

Molecular orbital calculations show that both the oxygen atoms and the *o*-carbon atoms are sites of high spin density for a large number of substituted nitrobenzene radical anions.[9b] Substitution of electron-donating groups increases the spin density at the oxygens and the *o*-carbons. In almost all cases the sign is positive (0.087 to 0.211 at the oxygen atoms and −0.017 to 0.147 at the *o*-carbon atoms for *m*-dinitrobenzene to *p*-aminonitrobenzene radical anions, respectively). The spin density at these sites for *o*-trifluoromethylnitrobenzene anion radicals is also probably positive. The substitution of either the methoxy, amino, or oxy (anion) groups in the *para* position is expected to similarly increase the spin density at both the oxygen and *o*-carbon atoms of the radical anions. Since these groups also increase the spin density on nitrogen the nitrogen hyperfine coupling is expected to increase in this series. Figure 7 shows a plot of the nitrogen and fluorine coupling constants (A_{N} and A_{F}) as a function of the Hammett σ constant. A fairly good linear relationship is obtained for A_{N}. This is in good agreement with previously obtained data on substituted nitrobenzene radical anions.[5,6,31]

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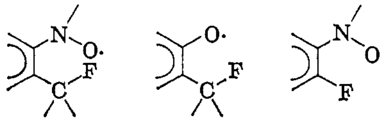
oxygen and fluorine since these atoms are connected through three carbons and one nitrogen in a six-membered ring.



A five-membered ring containing fluorine apparently does not lead to broadened lines since trifluoromethylbenzosemiquinone[17] and *o*-fluoronitrobenzene[11] radical anions give normal spectra. This would seem to eliminate fluorine p orbital interaction with the nitrogen p orbital. Since studies of fluoronitrobenzene radical anions were performed in alcohol solvents where lines are known to be generally sharper we have repeated this work in acetonitrile. Very similar spectra were obtained as shown in ref 11a. The line widths for the *ortho* isomer are greater than in the *meta* isomer but line-width alternation effects are not immediately apparent. For *o*-fluoronitrobenzene in acetonitrile $A_{\mathrm{N}} = 9.76$, $A_o{}^{\mathrm{F}} = 6.28$, $A_o{}^{\mathrm{H}} = 3.35$, $A_m{}^{\mathrm{H}} = 1.08$, $A_p{}^{\mathrm{H}} = 3.94$ gauss; for *m*-fluoronitrobenzene $A_{\mathrm{N}} = 9.22$, $A_o{}^{\mathrm{H}} = 3.11, 3.34$, $A_m{}^{\mathrm{F}} = 2.8$, $A_m{}^{\mathrm{H}} = 1.04$, $A_p{}^{\mathrm{H}} = 3.80$ gauss.

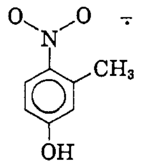
(29) Temperature studies of these spectra are in progress. Details will be published elsewhere.

(30) R. L. Ward, *J. Chem. Phys.*, **38**, 2588 (1963), and ref 11b. $A_{\mathrm{N}} = 16.05$, $A_{o-p} = 2.7$, $A_{\mathrm{F}} = 3.6$, $A_m = 1.1$ gauss.

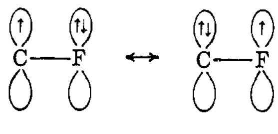
(31) The fact that a better fit to this line is obtained when σ for oxy (anion) is used rather than σ for hydroxy substantiates our earlier conclusion that the radical observed in the reduction of 4-hydroxy-2-trifluoromethylnitrobenzene is in fact the 4-oxy-2-trifluoromethylnitrobenzene dianion radical.

The magnitude of A_F however follows a smooth curve as a function of the Hammett σ. Although A_F is larger for the 4-methoxy and 4-amino derivatives than for the unsubstituted radical, A_F for the 4-oxy derivative is smaller than for the 4-methoxy and 4-amino analogs and approximately equal to A_F in the unsubstituted 2-trifluoromethylnitrobenzene radical. This result seems anomalous if the fluorine coupling is only proportional to the spin density on the contiguous ring carbon atom. However, if the fluorine coupling is greater because of a slower rotation of the trifluoromethyl group this result may be reasonable. Thus the strongly electron-donating *p*-amino and *p*-oxy (anion) group may cause the already negatively charged nitro group to twist out of the plane of the benzene ring. This effect is known to increase the nitrogen coupling.[5d] It would allow greater freedom of rotation for the *o*-trifluoromethyl group and thus reduce the effectiveness of spin transfer to the fluorine p orbitals. In fact the spectrum of 4-oxy-2-trifluoromethylnitrobenzene dianion radical could be interpreted in terms of a more freely rotating trifluoromethyl as compared to the unsubstituted radical or the *p*-methoxy and *p*-amino derivatives. This interpretation is consistent with either mechanism for hindrance to free rotation of the trifluoromethyl group since the sign of the spin densities at the oxygens and *o*-carbons is probably the same.

It should be noted that the spectrum of 4-hydroxy-2-methylnitrobenzene anion radical shows no unusual line-width variations or enhanced methyl hydrogen splitting: $A_N = 14.6$, $A_o{}^H = A^H{}_{O\text{-}CH_3} = 2.1$, $A_m{}^H = A_{OH} = 0.67$ gauss in acetonitrile. Thus a high spin density at the oxygens of the nitro group and the *ortho* ring carbons is not alone sufficient for interaction with neighboring atoms. Availability of p orbitals on the neighboring atoms seems a requirement for this type of spin interaction.



Trifluoromethyl Fluorine Coupling. The mechanism of fluorine coupling in fluorine-substituted radicals has already received some attention.[9f,11,32,33] All studies support the theory that spin transfer to fluorine p orbitals takes place and that the sign of the fluorine coupling is the same as the sign of the spin density on the attached carbon atom.



The following equation has been proposed to account for the magnitude of the observed fluorine coupling constants.[33]

$$A_F = Q^C{}_{CF}\rho_C + Q^F{}_{FC}\rho_F \qquad (1)$$

where ρ_C and ρ_F are the spin densities on the carbon and fluorine atoms, respectively, $Q^C{}_{CF}$ is the contribution to the fluorine coupling from configurational interaction, and $Q^F{}_{FC}$ is the contribution from spin density in a 2p orbital of fluorine.

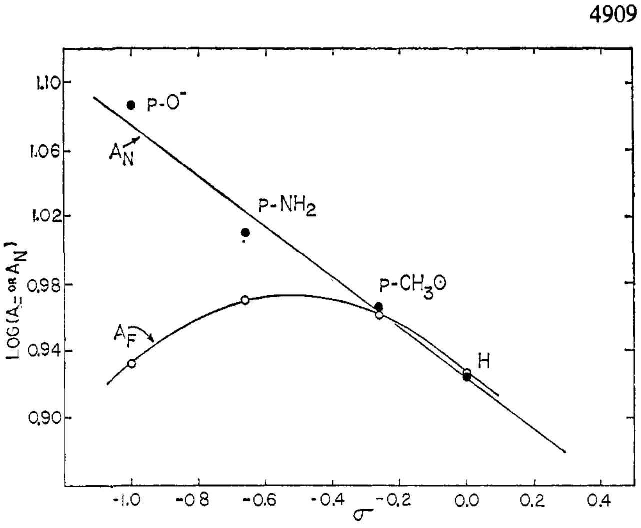


Figure 7. Plot of log A_N and log A_F as a function of the Hammett σ constant for 4-substituted 2-trifluoromethylnitrobenzene radical anions. σ Values for *p*-CH_3O and *p*-NH_2 were taken from J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p 172, and for *p*-O^- from J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 87. Other authors have -0.519 for *p*-O^- [*e.g.*, H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953)], but a value of -1.00 clearly fits our data better.

A similar equation for trifluoromethyl fluorine coupling is suggested by single-crystal studies of X-irradiated sodium perfluorosuccinate[34] and fluorine contact shifts in trifluoromethylphenylnickel(II) aminotroponeiminates[35]

$$A^F{}_{CF_3} = Q^C{}_{C\text{-}CF_3}\rho_C + Q^F{}_{FC}\rho_F \qquad (2)$$

where the first term accounts for fluorine splitting due to spin density in a 1s or 2s fluorine orbital brought about by spin polarization and where the second term accounts for fluorine splitting due to spin density in a fluorine p orbital. Eaton, *et al.*,[35] have shown that the magnitude of the trifluoromethyl fluorine coupling per unit spin density differs when the substitution is in the *para* and *meta* position. Thus in the equation

$$A_F = Q\rho_C \qquad (3)$$

$Q = +38.4$ and $+9.0$ in the *para* and *meta* position, respectively. In the trifluoromethylnitrobenzenes the magnitude of the fluorine coupling also changes depending on the site of substitution. Thus $A^F = 8.0$ and 1.2 gauss for the *para* and *meta* isomer, respectively. If the spin densities are taken as approximately 0.167 and -0.041 at the *para* and *meta* position of the trifluoromethylnitrobenzene radical anions[36] we obtain Q values for eq 3 of 48 and 29 for the *para* and *meta* positions. Possibly, as in the case of methyl hydrogen coupling in methyl-substituted radicals and radical ions,[37] charge plays an important role in determining the magnitude of fluorine coupling in trifluoromethyl-substituted radicals

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(32) D. H. Anderson, P. J. Frank, and H. S. Gutowsky, *J. Chem. Phys.*, **32**, 196 (1960); C. Trapp, C. S. Wang, and R. Filler, *ibid.*, **45**, 3472 (1966).

(33) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Mol. Phys.*, **5**, 407 (1962); D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips, and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4100 (1962); R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965).

(34) M. T. Rogers and D. H. Whiffen, *ibid.*, 40, 2662 (1964).

(35) D. R. Eaton, A. D. Josey, and W. A. Sheppard, *J. Am. Chem. Soc.*, **85**, 2689 (1963).

(36) Interpolated from ref 9b by use of Hammett's σ constants.

(37) J. R. Bolton, A. Carrington, and A. D. McLachlan, *Mol. Phys.*, **5**, 31 (1962).

and radical ions.[38] This consideration is under further investigation.

Experimental Section

Trifluoromethylnitrobenzene derivatives were obtained from Pierce Chemical Company and recrystallized or distilled before use. *p*-Trifluoromethylnitrobenzene was received as a gift from E. I. du Pont de Nemours and Company. 3-Methyl-4-nitrophenol was obtained from Aldrich Chemical Company. Acetonitrile was distilled from calcium hydride before use. Tetraethylammonium perchlorate was obtained from Eastman Organic Chemicals or made by a metathesis reaction in water from tetraethylammonium bromide and ammonium perchlorate.

Nitrobenzene radical anions were generated electrolytically *in situ* in a Varian flat cell in the cavity of a Varian 4502 epr spectrometer. This system includes a 12-in. magnet with Fieldial control. The coupling constants were calculated from the scan rates specified on the Fieldial control and scanning unit. High-resolution spectra were obtained by using 100-min scans.

Electrolytic reduction was carried out in a system very similar to that originally described by Geske and Maki.[5a] Although the mercury–calomel electrode system was adequate for stable radicals it was found that for unstable radicals such as 4-methoxy- and 4-hydroxy-2-trifluoromethylnitrobenzene the rate of production of radicals was too slow to maintain a high enough steady concentration of radicals for long scanning periods. This result seem to be related to concentration polarization of the electrode. Multistranded wire, *e.g.*, Belden 20AWG 10 × 30, gave excellent results when the electrode was separated from the bulk of the solution by a fritted glass disk. This arrangement was used for most reductions. No attempt was made to measure the reduction potential simultaneously with free-radical production. Typical values for nitrobenzene derivatives can be found in ref 5. In every experiment the applied voltage was slowly increased in small increments until the first radical was detected. This voltage was approximately the same as required to obtain the well-known spectrum of nitrobenzene radical anion.

Acknowledgment. We thank W. A. Sheppard of E. I. du Pont de Nemours and Company for providing us with a sample of *p*-trifluoromethylnitrobenzene and E. T. Strom for helpful discussions regarding this work. We also appreciate receiving a copy of Professor Watson's paper, prior to publication, describing similar work on trifluoromethylnitrobenzene anion radicals.

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[38] J. P. Colpa and J. R. Bolton, *Mol. Phys.*, **5**, 273 (1962).

Chemical Shift Nonequivalence of Diastereotopic Protons Due to Restricted Rotation around Aryl–Nitrogen Bonds in Substituted Amides

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Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. *Received February 27, 1967*

Abstract: Chemical shift nonequivalence of diastereotopic protons in cyclic and acyclic amides and several related systems is interpreted within the framework of the conformational analysis of mobile systems. An approach to a critical discussion of kinetic and thermodynamic restrictions on ring flipping, torsional, and inversional modes of conformational interchange is developed. The chemical shift nonequivalence of the diastereotopic benzyl methylene protons in N-benzyl-N-(*o*-tolyl)acetamide has been reinvestigated within this general framework. Analysis of the nmr spectra of a variety of cyclic and acyclic amides indicates that a previous interpretation which viewed this phenomenon as arising from slow inversion of pyramidal amide nitrogen is in error. A more reasonable alternative is presented, that the source of the nonequivalence lies in restricted rotation about the aryl–nitrogen bond. Coalescence temperatures indicate free energies of activation for this process of 20.0 and 17.3 kcal/mole for N-benzyl-N-(*o*-tolyl)acetamide and N-*o*-tolyl-1,4-dihydro-3(2*H*)-isoquinolinone, respectively. The possibility of cisoid–transoid isomerism about the nitrogen–carbonyl bond is also discussed, and assignments of configuration of the *s-cis* and *s-trans* isomers of N-benzyl-N-(*o*-tolyl)formamide have been made, using aromatic solvent-induced shifts.

The work described in this paper was prompted by the appearance of a recent claim by Siddall and Prohaska[2] that the chemical shift nonequivalence, at ordinary temperatures, of the methylene protons in N-benzyl-N-(*o*-tolyl)acetamide (**2**, Table I) constituted evidence for "slow inversion at the nitrogen atom" in this amide. However, it has been known for some time[3] that the pyramidal H_2NC group in formamide suffers *rapid* inversion, similar to the wagging motion in ammonia, with an activation energy barrier of only about 1 kcal/mole. The low barrier for pyramidal inversion in this and similar amides[4] is inconsistent with the conclusion[2] that the inversion in **2** "must be less rapid than the mean lifetime of something like 1–10 msec." Further, the observed[2] chemical shift equivalence of the methylene protons in N-benzyl-N-(2,6-dimethylphenyl)acetamide and in N-benzylacetanilide, assuming that the appearance of a singlet is not the result of accidental chemical shift coincidence, would be difficult to understand if slow inversion at

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[1] (a) Institute of Chemistry, Tel-Aviv University, Ramat-Aviv, Israel. (b) Supported by a grant (CA-02551) to Princeton University from the National Cancer Institute, National Institutes of Health. (c) Supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-67.

[2] T. H. Siddall and C. A. Prohaska, *Nature*, **208**, 582 (1965).

[3] C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, **32**, 158 (1960).

[4] In nitramide and cyanamide, the corresponding barriers are 2.7 and 2.0 kcal/mole, respectively [J. K. Tyler, J. Sheridan, and C. C. Costain, unpublished work, cited by P. G. Lister and J. K. Tyler, *Chem. Commun.*, 152 (1966)]. In the crystalline state, amides are said to be planar or nearly so (S. C. Nyburg, "X-Ray Analysis of Organic Structures," Academic Press Inc., New York, N. Y., 1961, p 191 ff).