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An Electron Spin, ENDOR, and TRIPLE Resonance and INDO Study of Fluorine-substituted *N,N'*-Diphenyl-4,4'-bipyridylium Radical Cations

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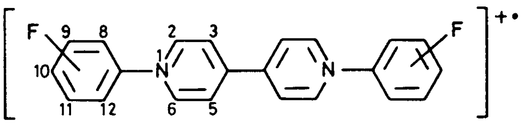
E.s.r., ENDOR, and TRIPLE resonance results are reported for the radical cation of *N,N'*-diphenyl-4,4'-bipyridylium dichloride and a series of its fluorophenyl analogues. The effect of *ortho*-, *meta*-, and *para*-substitution on the spin density distribution within the molecule is discussed and the observed coupling constants for the fluorine-substituted phenyl derivatives are analysed with the aid of INDO molecular orbital calculations. The magnitude of the spin delocalised into the phenyl rings when *ortho*-substituted suggests that these rings are substantially twisted with respect to the plane of the bipyridylium rings.

Recent studies[1,2] have shown that the substituent group on the nitrogen atom of bipyridyl plays an important part in determining the unpaired electron distribution in the radical cation. In this paper we extend this work to a study of how the unpaired spin density distribution is affected by ^{19}F substitution in the phenyl group of phenyl-substituted bipyridylium compounds. The structure and numbering system is shown in (**1**).



(1)

Experimental

Materials.—*N,N'*-Diphenyl-4,4'-bipyridylium dichloride (DPB) was kindly provided by I.C.I. *N,N'*-Bis-(2-fluorophenyl)-4,4'-bipyridylium dichloride (8-FPB), *N,N'*-bis-(3-fluorophenyl)-4,4'-bipyridylium dichloride (9-FPB), *N,N'*-bis-(4-fluorophenyl)-4,4'-bipyridylium dichloride (10-FPB), *N,N'*-bis-(2,6-difluorophenyl)-4,4'-bipyridylium dichloride (8,12-DFPB), *N,N'*-bis-(2,4-difluorophenyl)-4,4'-bipyridylium dichloride (8-10-DFPB), *N,N'*-bis-(2,4,6-trifluorophenyl)-4,4'-bipyridylium dichloride (8,10,12-TFPB), *N,N'*-bis-(2,3,4,6-tetrafluorophenyl)-4,4'-bipyridylium dichloride (8,9,10,12-TFPB), *N,N'*-bis-(2,3,5,6-tetrafluorophenyl)-4,4'-bipyridylium dichloride (8,9,11,12-TFPB), and *N,N'*-bis-(2,3,4,5,6-pentafluorophenyl)-4,4'-bipyridylium dichloride (PFPB) were all prepared by a method similar to that of Allen[3] except that the appropriate halogenated aniline was used as the starting material. The structures and purities were determined by ^{1}H and ^{19}F n.m.r. and CHN analysis.

Procedure.—Methanolic solutions of the radical cation (*ca.* 10^{-4}M) were prepared by passing the solution of the diquaternary salt over freshly prepared zinc metal films or by photolysis under anaerobic conditions as described earlier.[2] There was no difference in e.s.r. or ENDOR spectra obtained by the two methods. E.s.r. experiments were carried out with a Varian E109 spectrometer and ENDOR experiments with a Bruker ENDOR instrument interfaced to the E109.

Results and Discussion

E.s.r., ENDOR and TRIPLE Resonance Spectra.—All the radical cations solutions were green in colour and stable for several weeks. Figure 1 shows the e.s.r. spectrum of the *N,N'*-bis-(2,4,6-trifluorophenyl)-4,4'-bipyridylium radical cation (8,10,12-TFPB$^{+\cdot}$) recorded at room temperature; Figures 2(a) and 2(b) show the ENDOR and general TRIPLE spectra recorded at −70 °C as examples. The e.s.r. spectral intensity decreased with decreasing temperature as found previously for other similar radical cations.[2,4] The hyperfine coupling constants are given in Table 1.

Assignments of the Hyperfine Coupling Constants.—*Nitrogen.* The nitrogen coupling constants were obtained from the e.s.r. spectra. Measurements of the nitrogen coupling constant using ENDOR techniques could not be made for these radical cations because no ENDOR absorptions were detected even at temperatures higher than that (−70 °C) at which fluorine and proton ENDOR occurred. The use of other solvents (at room temperature) such as trifluoroacetic acid did not help in detecting the nitrogen ENDOR absorptions although under similar conditions such absorptions have been clearly detected from radical cations derived from 2,2'-bipyridylium diquarternary salts.[5]

Pyridyl protons. The assignments of the pyridyl proton coupling constants (positions 2 and 3) have been made previously for the unsubstituted radical cation (DPB.$^{+\cdot}$).[1] Selective deuteriations were also carried out to confirm by both e.s.r. and ENDOR that this assignment holds for all these substituted phenyl radical cations.[6]

Phenyl protons. These assignments for the substituted compounds were made by comparison with DPB$^{+\cdot}$ and each other.

For the 8-FPB radical cation the largest phenyl coupling constant was assigned to the remaining *ortho*-proton (position 12). The *meta*-protons, which become inequivalent in this case, showed two different experimental coupling constants. The larger was similar in magnitude to that of the *meta*-proton of DPB$^{+\cdot}$ and therefore was assigned to the *meta*-proton at position 11; the smaller was assigned to position 9.

In the radical cation of 9-FPB the couplings of protons at positions 8, 10, and 12 were similar in value to those of DPB$^{+\cdot}$ and were assigned accordingly. The remaining proton coupling therefore can only be assigned to position 11. The assignment of the coupling constants in 10-FPB$^{+\cdot}$ has been reported previously.[1,4]

The hyperfine coupling constants for the *para*- and *meta*-protons of 8,12-DFPB$^{+\cdot}$ were very similar in absolute magnitude; however, these were differentiated by general TRIPLE resonance experiments as they were opposite in sign. For the radical cation of 8,10-DFPB we assigned the largest phenyl proton coupling to the *ortho*-position (12) because of its negative sign; the remaining two positive couplings were assigned to the two *meta*-positions. The smaller of the two we assigned to position 9, *i.e.* between the two ^{19}F substituents, and the larger was assigned to position 11.

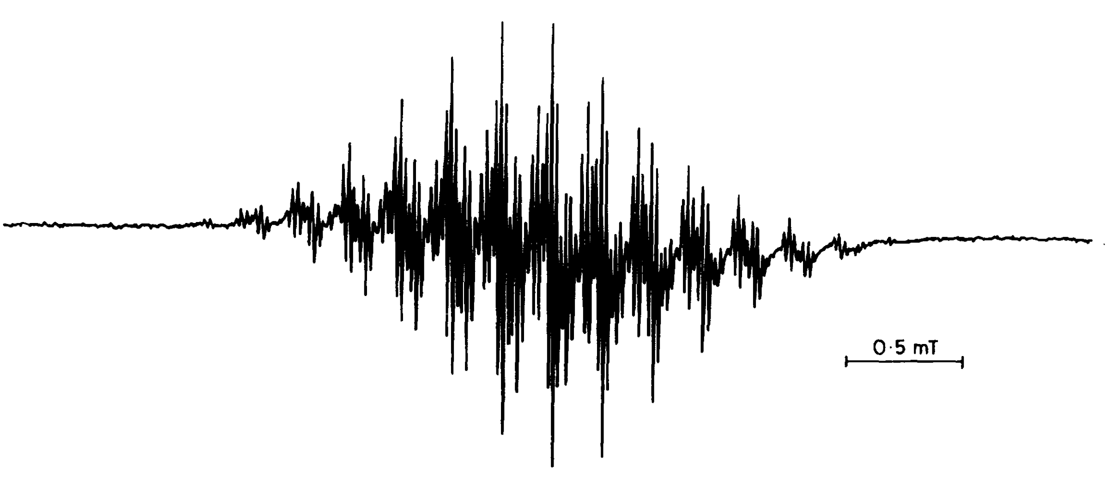


Figure 1. E.s.r. spectrum of 8,10,12-TFPB$^{+\cdot}$ in methanol at room temperature

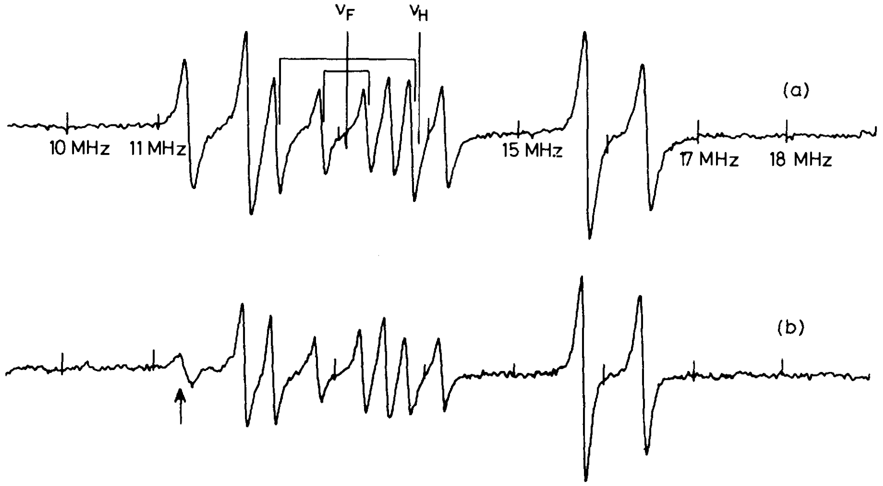


Figure 2. (a) ENDOR spectrum of 8,10,12-TFPB$^{+\cdot}$ in methanol at −70 °C; (b) general TRIPLE spectrum of 8,10,12-TFPB$^{+\cdot}$ in methanol at −70 °C ('pumped' frequency indicated by an arrow)

The assignment of the phenyl couplings constants is unambiguous for 8,9,10,12-TFPB and 8,9,11,12-TFPB.

Fluorine. For the radical cation of 8,10-DFPB two ^{19}F ENDOR absorptions were obtained; the larger was assigned to the *para*-position (10) because of its magnitude and positive sign. The assignment of the fluorine coupling constant of 8,12-DFPB$^{+\cdot}$ was also unambiguous since the ENDOR-observed coupling constant can only be assigned to the equivalent *ortho*-fluorine nuclei. General TRIPLE resonance experiments showed that these *ortho*-fluorine atoms have a sign (negative) for the hyperfine coupling constant similar to that of the replaced protons. The *para*-fluorine atoms on the other hand have a hyperfine coupling with a positive sign which is opposite to that of the replaced protons.

Fluorine coupling constants for the 8,10,12-TFPB radical cation were assigned by comparison with the 10-FPB and the 8,12-DFPB radical cations.

In the case of the 8,9,11,12-TFPB radical cation the fluorine coupling constants were all similar in magnitude and were very small; however, they consisted of two pairs opposite in sign and were assigned on the basis of this fact and by comparison with the others. For the 8,9,10,12-TFPB radical cation the largest ^{19}F coupling (positive) was assigned to the 10-positon. The smallest ^{19}F coupling constant was then assigned to the 8- and 12-position and the remaining value to the 9-position on the basis of relative signs.

For the pentafluoro-substituted radical cation the assignments were made by comparison with the other ^{19}F-substituted radical cations.

All these values with their assignments are shown in Table 1.

Effects of para- *and* meta-*Substitution.*—Fluorine substitution in the *meta*- or *para*-position of the phenyl ring appears to have little effect on the spin density distribution as compared with the diphenylbipyridylium radical cation (DPB$^{+\cdot}$). The a_F/a_H value of 2.25 for *para*-fluorine substitution (10-FPB$^{+\cdot}$) is in good agreement with that reported for other radicals.[7,8]

Similar a_F/a_H values are also observed for fluorine substitution at the *para*-position for the other radicals studied here. Thus, fluorine substitution at the *para*-position of 8-FPB$^{+\cdot}$ giving 8,10-DFPB$^{+\cdot}$ has a fluorine–proton coupling constant ratio of 2.095:1. Similarly a ratio of 2.00:1 is obtained for the fluorine–proton coupling constants of 8,12-DFPB$^{+\cdot}$ and 8,10,12-TFPB$^{+\cdot}$. This feature is also evident for 8,9,11,12-TFPB$^{+\cdot}$ and 8,9,10,11,12-PFPB$^{+\cdot}$ where a fluorine–proton coupling constant ratio of 2.37:1 is obtained.

Whereas substitution of a fluorine atom for a proton at the *para*-position produces a fluorine hyperfine coupling constant

Table 1. Coupling constants of fluorinated *N,N'*-diaryl-4,4'-bipyridylium radical cations

Radical cation	Hyperfine coupling constants (mT) 1	2	3	8	9	10	11	12
DPB$^{+\bullet}$	+0.380	−0.159	−0.140	−0.054	+0.031	−0.050	+0.031	−0.054 (ref. 1)
8-FPB$^{+\bullet}$	+0.365	−0.171	−0.140	−0.010*	+0.023	−0.038	+0.030	−0.048
9-FPB$^{+\bullet}$	+0.377	−0.164	−0.136	−0.055	+0.007*	−0.048	+0.028	−0.055
10-FPB$^{+\bullet}$	+0.380	−0.161	−0.141	−0.050	+0.030	+0.116*	+0.030	−0.050 (ref. 3)
8,10-DFPB$^{+\bullet}$	+0.368	−0.171	−0.139	−0.010*	+0.021	+0.077*	+0.027	−0.045
8,12-DFPB$^{+\bullet}$	+0.345	−0.183	−0.137	−0.014*	+0.023	−0.027	+0.023	−0.014*
8,10,12-TFPB$^{+\bullet}$	+0.359	−0.184	−0.136	−0.018*	+0.021	+0.054*	+0.021	−0.018*
8,9,10,12-TFPB$^{+\bullet}$	+0.344	−0.189	−0.133	−0.014*	+0.024*	+0.065*	+0.018	−0.014*
8,9,11,12-TFPB$^{+\bullet}$	+0.340	−0.193	−0.128	−0.004*	+0.004*	−0.029	+0.004*	−0.004*
8,9,10,11,12-PFPB$^{+\bullet}$	+0.340	−0.194	−0.128	−0.009*	+0.009*	+0.069*	+0.009*	−0.009*

[a] An asterisk denotes ^{19}F.

Table 2. INDO-Calculated coupling constants (mT)[a,b]

Radical cation	Twist angle[c]	1	2,6[d]	3,5[d]	8	9	10	11	12
DPB$^{+\bullet}$	0	0.451	−0.125	−0.101	−0.081	0.029	−0.058	0.029	−0.081
	20	0.456	−0.121	−0.104	−0.073	0.030	−0.052	0.030	−0.073
	40	0.470	−0.114	−0.112	−0.054	0.032	−0.037	0.032	−0.054
	60	0.487	−0.107	−0.119	−0.037	0.032	−0.019	0.032	−0.037
8-FPB$^{+\bullet}$	0	0.448	$-0.131^{(2)}$ $-0.125^{(6)}$	$-0.110^{(3)}$ $-0.094^{(5)}$	0.152*	0.026	−0.058	0.030	−0.086
	20	0.452	$-0.126^{(2)}$ $-0.122^{(6)}$	$-0.111^{(3)}$ $-0.098^{(5)}$	0.188*	0.025	−0.051	0.031	−0.078
	40	0.466	$-0.117^{(2)}$ $-0.116^{(6)}$	$-0.114^{(3)}$ $-0.108^{(5)}$	0.134*	0.025	−0.036	0.032	−0.059
	60	0.482	$-0.111^{(2)}$ $-0.110^{(6)}$	$-0.119^{(3)}$ $-0.116^{(5)}$	0.013*	0.024	−0.017	0.031	−0.042
8,12-DFPB$^{+\bullet}$	0	0.444	−0.131	−0.103	0.143*	0.029	−0.058	0.029	0.143*
	20	0.438	−0.125	−0.103	0.170*	0.025	−0.049	0.025	0.170*
	40	0.450	−0.118	−0.108	0.112*	0.024	−0.033	0.024	0.112*
	60	0.465	−0.113	−0.113	−0.009*	0.023	−0.015	0.023	−0.009*
9-FPB$^{+\bullet}$	0	0.442	−0.132	−0.097	−0.081	−0.107*	−0.056	0.028	−0.081
10-FPB$^{+\bullet}$	0	0.456	−0.120	−0.103	−0.082	0.030	0.166*	0.030	−0.082

[a] Interannular bond distance 1.40 Å, N–C(7) bond distance 1.42 Å, angles C(7)C(8)H(8) = C(7)C(8)F(8) = 120°, NC(2)H(2) = 126°, C(2)C(3)H(3) = 114°, C(8)C(9)F(9) = 120°. [b] An asterisk denotes fluorine hyperfine coupling constants. [c] Angle between the phenyl and the pyridyl ring planes. [d] Numerical superscripts in parentheses refer to positions in the pyridyl ring for 8-FPB$^{+\bullet}$.

twice that of the replaced proton, *meta*-fluorine substitution shows different results. For example a fluorine–proton coupling constant ratio of 0.26:1 is obtained from 9-FPB$^{+\bullet}$, whereas a much larger ratio (1.35:1) is observed for 8,9,10,12-TFPB$^{+\bullet}$. In addition a ratio of only 0.37:1 is obtained for the *meta*-F position in PFPB$^{+\bullet}$ and the *meta*-proton in 8,10,12-TFPB$^{+\bullet}$. Different *meta* a_F/a_H values have also been reported by other workers.[8,9]

Molecular Orbital Calculations (*INDO*).—INDO molecular orbital calculations on DPB$^{+\bullet}$ have been used to aid in the assignments and to determine the absolute signs of the hyperfine coupling constants. These calculations suggest that the *ortho*-protons have the largest phenyl hyperfine coupling constant, followed by the *para*-protons, while the *meta*-protons give the smallest hyperfine coupling constant. The calculations also show that the *ortho*- and *para*-protons have a similar sign to that of the pyridyl protons (negative) and that the *meta*-proton coupling constant has an opposite sign (positive). Similar results were obtained from general TRIPLE resonance experiments.

INDO molecular orbital calculations carried out on 8-FPB$^{+\bullet}$ (see Table 2) show that the *ortho*-proton hyperfine coupling constant is always larger than that of the *para*-, and that the *meta*-proton of position 11 has a slightly larger hyperfine coupling constant than the *meta*-proton of position 9. The INDO results for 8-FPB$^{+\bullet}$, 9-FPB$^{+\bullet}$, 10-FPB$^{+\bullet}$, and 8,12-DFPB$^{+\bullet}$ are all shown in Table 2. Reasonable agreement is observed between the calculated and experimental ^{19}F and ^{1}H coupling constants for the *meta*- and *para*-positions.

Effect of ortho-*Substitution*.—The introduction of a large substituent into the *ortho* position has a great effect on the spin density distribution in the radical cation.[1,2] Thus single *ortho*-fluorine substitution (8-FPB$^{+\bullet}$) causes a significant decrease in the hyperfine coupling constants of both the *para*- and the remaining *ortho*-protons. When all the *ortho*-protons are replaced by fluorine (8,12-DTPB$^{+\bullet}$) the *para*-proton (position 10) hyperfine coupling constant is almost halved in value. The most reasonable explanation of this effect, based on molecular orbital calculations and molecular models, is that steric interactions between the *ortho*-fluorine atoms and the 2-pyridyl protons cause a twisting of the substituted phenyl rings from the plane of the two pyridyl rings. Consequently the phenyl rings become less conjugated with the rest of the molecule and as a result the spin density at the *ortho*- and *para*-carbon atoms is reduced. Substitution of a chlorine atom (8-CPB$^{+\bullet}$)[6] at the *ortho*-position causes both *para*- and *ortho*-protons to have

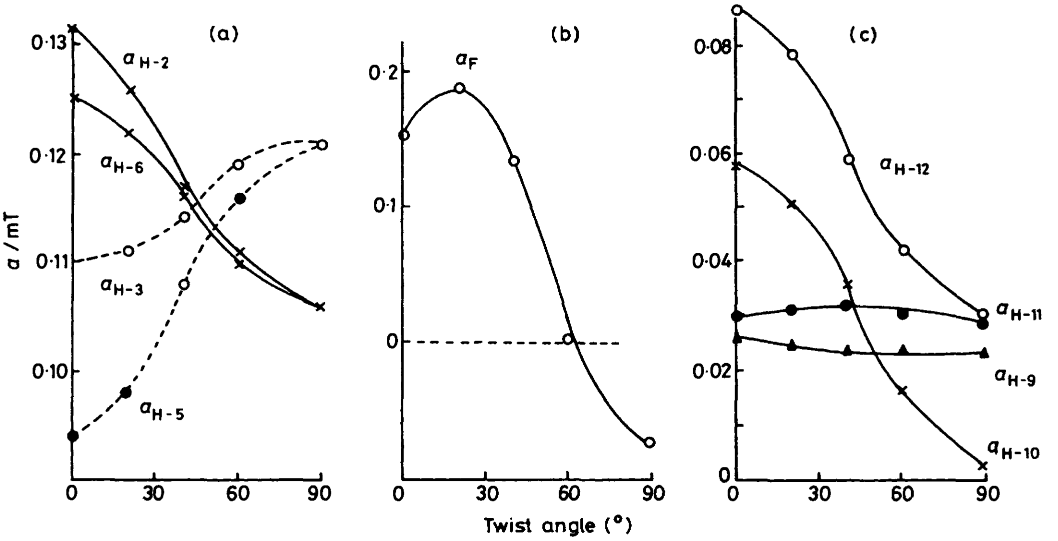


Figure 3. Effect of twisting the phenyl rings out of the bipyridyl plane on the hyperfine coupling constants; values in mT (from INDO calculations) irrespective of sign for 8-FPB$^{+\cdot}$: (a) variation in the pyridyl couplings 2 and 3 (values are negative); (b) variation in the ^{19}F coupling (positive changing to negative); (c) variation in the phenyl couplings for 9,10,11, and 12 (values for 10 and 12 are negative, for 9 and 11 are positive)

much smaller hyperfine coupling constants than those observed in 8-FPB$^{+\cdot}$ or even 8,12-DFPB$^{+\cdot}$.[6] This implies that the amount of twist caused by a single *ortho*-chlorine is greater than that produced by two *ortho*-fluorine atoms. Replacing the chlorine by bromine[6] (8-BPB$^{+\cdot}$) or iodine[6] (8-IPB$^{+\cdot}$) will produce more twist and hence less conjugation between the phenyl and the bipyridylium rings (*cf.* absorptions 8-CPB$^{+\cdot}$ 403 nm, 8-BPB$^{+\cdot}$ 400 nm, 8-IPB$^{+\cdot}$ 398 nm), which in turn leads to even smaller *ortho*- and *para*-proton hyperfine coupling constants. It can be seen from Table 1 that this *ortho*-substitution does not seriously affect the hyperfine coupling constants of the *meta*-protons since the spin density at the *meta*-carbon atoms is mainly due to spin polarization, which is not affected by twisting the phenyl ring.

The visible–u.v. spectra of these radical cations provide further evidence to support this hypothesis. Conjugation in the radical cation molecule (DPB$^{+\cdot}$) is not affected by *meta*- or *para*-substitutents; thus DPB$^{+\cdot}$, 9-FPB$^{+\cdot}$, and 10-FPB$^{+\cdot}$ absorb at the same wavelength (432 nm). Single *ortho*-fluorine substitution, which reduces the conjugation in the radical, shifts the absorption to shorter wavelength (414 nm). The addition of another *ortho*-fluorine (8,12-DFPB$^{+\cdot}$) shifts the absorption peak further towards shorter wavelength (406 nm) as the twist is increased. As expected the twist caused by a single *ortho*-chlorine is larger than that caused by two *ortho*-fluorine atoms, as 8-CPB$^{+\cdot 6}$ absorbs at a slightly shorter wavelength (403 nm) than 8,12-DFPB$^{+\cdot}$.

Figure 3 shows the dependence of all the calculated coupling constants on twist angle between the phenyl rings and the plane of the bipyridyl rings for 8-FPB$^{+\cdot}$. The inferences drawn from the experimental results for all the substituted radical cations appear to be satisfactorily explained. Thus, the two *meta*-proton coupling constants are significantly different from each other and are approximately unchanged on twisting the phenyl rings. On the other hand both *ortho*- and *para*-proton coupling constants change dramatically on rotating from in plane (0°) to perpendicular (90°).

The effect of *ortho*-fluorine substitution on the experimental pyridyl proton hyperfine coupling constants is remarkable. The a_{H-2}/a_{H-3} value of 1.14 for the unsubstituted radical cation (DPB$^{+\cdot}$) is increased by a single *ortho*-fluorine substitution to 1.22. The presence of two *ortho*-fluorine nuclei has a much greater effect: this value is further increased to 1.33. Increasing the number of fluorine atoms in the phenyl ring further increases the value to 1.52 in PFPB$^{+\cdot}$.

Table 3. Dependence of a_{H-2}/a_{H-3} on fluorine substitution and ring twist angle from INDO calculations

Twist angle	DPB$^{+\cdot}$	8-FPB$^{+\cdot}$	8,12-DFPB$^{+\cdot}$
0°	1.24	1.25	1.27
20°	1.16	1.19	1.21
40°	1.02	1.05	1.09
60°	0.90	0.94	1.00

Since one might expect a maximum twist to be produced by the presence of only two *ortho*-fluorine nuclei (8,12-DFPB$^{+\cdot}$), twisting the phenyl ring is not therefore completely responsible for increasing the a_{H-2}/a_{H-3} value, as this continues to rise on adding more fluorine atoms to the *meta*- and *para*-positions. Moreover, replacing fluorine by chlorine, bromine, or iodine does not increase the value, even though the degree of twist is expected to be greater.

In fact Figure 3 shows that rotation of the phenyl rings out of plane increases a_{H-3} but decreases a_{H-2}, thereby reducing a_{H-2}/a_{H-3}. It is clear that two opposing effects are in operation. In addition to rotation of the phenyl rings, which reduces a_{H-2}/a_{H-3}, substitution of electron-withdrawing fluorine atoms into the phenyl rings gives rise to an increase in this. These two factors are nicely illustrated in Table 3, which shows the changes in the INDO-calculated a_{H-2}/a_{H-3} values with twist angle for DPB$^{+\cdot}$, 8-FPB$^{+\cdot}$, and 8,12-DFPB$^{+\cdot}$. The experimental results suggest that the electron-withdrawing effect dominates the steric (twisting) factor and although the calculations reproduce the correct trends, they appear to underestimate the former contribution.

The effect of substituting large groups of electron-donating character (*e.g.* methyl) into the *ortho*-position of the phenyl ring has previously been demonstrated.[2] In this case both steric and electronic effects of the methyl group are operating in the same direction. Thus one *ortho*-methyl group causes a_{H-2}/a_{H-3} to decrease to 1.06, while the presence of two *ortho*-methyl groups reduces its value to unity. In this case INDO calculations satifactorily account for the observed value of $a_{\text{H-2}}/a_{\text{H-3}}$.

Interestingly, for 8-FPB$^{+\bullet}$ the calculations predict significant differences in spin densities within the two sets of pyridyl protons. In particular the calculated coupling constants for the *meta*-protons (positions 3 and 5) are computed to differ by about 0.007 mT even at a rotation angle of 40°. The fact that these differences are not detected in the ENDOR experiment suggests that there is a rapid oscillation about the N–phenyl bond.

The *ortho*-fluorine coupling constants are experimentally much smaller than would be expected from a comparison with the *ortho*-proton coupling constant in the unsubstituted radical or even in the mono-*ortho*-substituted radical cation (8-FPB$^{+\bullet}$). Small fluorine and proton coupling constants observed by Allendoerfer and Maki[8] in (*o*-fluorophenyl)diphenylmethyl and (*o*-tolyl)diphenylmethyl radicals have also been attributed to the lack of conjugation caused by steric forces between the *ortho*-fluorine or methyl and the *ortho*-protons. This *ortho*-effect has also been observed in tris-(2,6-difluorophenyl)methyl radical by Kulkarni and Trapp[10] and in the 2-fluorobenzophenone radical anion by Lubitz *et al.*[11] In the latter case both McLachlan and INDO molecular orbital calculations failed to account for the small *ortho*-fluorine coupling constant.

The INDO calculations indicate [Figure 3(b)] that the magnitude of this coupling constant depends critically on the angle of twist about the N–phenyl bond, with its value changing sign at a twist angle of about 60°. In addition it should be noted that these fluorine coupling constants are derived from extremely small spin densities, due to the very large fluorine electron-nuclear constant. The calculated value of 0.125 mT in the planar conformation is close to that normally anticipated for simple replacement of a hydrogen by a fluorine atom.

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