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# BONDING INFORMATION IN TUNGSTEN(VI) COMPOUNDS FROM DIRECTLY BONDED FLUORINE AND FLUOROPHENOXY SUBSTITUENTS

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## SUMMARY

The series of compounds $(FC_6H_4O)_nWF_{6-n}$, where n = 1-6 and F is *meta* or *para* to oxygen, has been prepared and all fluorine nmr chemical shifts determined. The W-F, *para*-F, and *meta*-F resonances all shift upfield as a function of n with approximate relative sensitivities of 1, 1/20, and 1/30, respectively. All chemical shifts are also found to be sensitive to molecular stereochemistry, with substituents *trans* to oxygen shifted to higher field than those *trans* to fluorine. $^{19}F$ data is also reported for the complete series $(C_6H_5O)_nWF_{6-n}$

## INTRODUCTION

Fluorine nmr chemical shifts are very sensitive indicators of changes in the chemical environment around the resonant nucleus. This fact, coupled to the minimal difficulties encountered in the observation of $^{19}F$ nmr signals, has resulted in the collection of large amounts of data and in the development of several correlations between chemical shifts and bond properties in fluorine containing molecules [1]. These correlations have involved measurements of two general types. The first were shifts of fluorine nuclei bound directly to the central atoms of interest, exemplified by Gutowsky's early work on binary fluorides in which a general correlation of chemical shift and electronegativity was often observed [2]. The second class involves $^{19}F$ shifts of fluorine nuclei several bonds removed from the central atom or site of molecular substitution. The substituted fluorobenzene correlations of Taft *et al.* typify this type of treatment [3]. Both of these correlation procedures are subject to criticism on the basis of oversimplification [4], but it would appear that reliable calculations of $^{19}F$ chemical shifts for large molecules are still somewhat in the future and so empirical schemes are likely to be of value for some time.

The development of a general method for the synthesis of compounds of the type $(RO)_nWF_{6-n}$ [5,6] has made available a series of closely related compounds in which one can have both types of fluorine nuclei mentioned above in one molecule, thereby facilitating a comparison of the bonding information derived from the two distinct substituent sites. An indication of the information which can be gained was obtained in the $^{19}F$ nmr study of $ArOWF_5$ molecules, with Ar = *p*-$FC_6H_4$, *m*-$FC_6H_4$, and $C_6F_5$ [7]. In these compounds the W-F fluorines are shifted upfield from $WF_6$, the axial fluorine more than the equatorial, and the Ar-F shifts indicate that in the Taft sense, $OWF_5$ is a strongly $\sigma$ and weakly $\pi$-withdrawing group. In the present study we have prepared and examined all the compounds $(ArO)_nWF_{6-n}$ where Ar is *m*-$FC_6H_4$ or *p*$FC_6H_4$ and n = 1-6, and have compared the bonding predictions which can be made from the chemical shift trends in each series of compounds.

## RESULTS AND DISCUSSION

The $^{19}F$ chemical shifts and coupling constants are collected in Tables 1 and 2.

### Fluorines bound directly to tungsten

There are now several series of compounds $(RO)_nMF_{6-n}$ for which $^{19}F$ chemical shift data have been collected. These include M = Sn [8], Te [9], and W [5,6,10]. These compounds are very likely similar structurally, but the chemical shift differences from series to series are quite pronounced. The main group element methoxy fluorides show much smaller chemical shift changes within a series. The range for tellurium is 22 ppm, for tin a range of 9.3 ppm is calculated [8]. In contrast, the shift range is over 200 ppm for the methoxy fluorides of tungsten and 145 ppm for the fluorophenoxy compounds in this study. The tellurium and tungsten series are the most directly comparable, both being neutral hexavalent molecules The (n-1) d orbitals of tellurium(VI) are filled while those of tungsten (VI) are empty. Since both fluoride and phenoxide are potentially π-donating from their lone pairs of electrons as well as σ-donating substituents, the tungsten(VI) molecules, which have available acceptor orbitals (dxy, dyz, dxy), provide a means for interaction between oxygen and fluorine which is absent in tellurium. The fact that the chemical shift range is

TABLE 1

NMR data for $(FC_6H_4O)_nWF_{6-n}$ molecules

| Compound | $\delta WF_{\underline{A}}^{a}$ | $\delta WF_{\underline{B}}^{a}$ | $J_{F_A-F_B}{}^{b}$ | $\delta ArF_{\underline{A}}^{c}$ | $\delta ArF_{\underline{B}}^{c}$ |
|---|---|---|---|---|---|
| $p\mathrm{FArOWF}_5$ | 37.9 | 47.0 | 64.4 | -57.31 | - |
| *cis*$(p\mathrm{FArO})_2\mathrm{WF}_4$ | 75.2 | 77.4 | 64.5 | -52.75 | - |
| *fac*$(p\mathrm{FArO})_3\mathrm{WF}_3$ | - | 102.2 | - | -49.46 | - |
| *mer*$(p\mathrm{FArO})_3\mathrm{WF}_3$ | 95.9 | 105.2 | 61 | -50.05 | -48.89 |
| *cis*$(p\mathrm{FArO})_4\mathrm{WF}_2$ | - | 126.1 | - | -47.66 | -46.91 |
| $(p\mathrm{FArO})_5\mathrm{WF}$ | - | 144.2 | - | -46.43 | -45.57 |
| $(p\mathrm{FArO})_6\mathrm{W}$ | - | - | - | - | -44.56 |
| $m\mathrm{FArOWF}_5$ | 35.7 | 44.1 | 64.6 | -55.77 | - |
| *cis*$(m\mathrm{FArO})_2\mathrm{WF}_4$ | 69.8 | 72.2 | 64.5 | -54.41 | - |
| *fac*$(m\mathrm{FArO})_3\mathrm{WF}_3$ | - | 95.6 | - | -53.46 | - |
| *mer*$(m\mathrm{FArO})_3\mathrm{WF}_3$ | 89.0 | 98.4 | 62 | -53.77 | -52.91 |
| *cis*$(m\mathrm{FArO})_4\mathrm{WF}_2$ | - | 118.8 | - | -53.07 | -52.30 |
| $(m\mathrm{FArO})_5\mathrm{WF}$ | - | 134.6 | - | -52.76 | -52.03 |
| $(m\mathrm{FArO})_6\mathrm{W}$ | - | - |  | - | -51.71 |

a. PPM upfield from external $WF_6$. Shifts measured from 25.0 KHz lower sideband of internal $C_6F_6$, plus 34.28 ppm. The estimated accuracy from one sample tube to another is ±1 ppm.
b. Coupling constants in Hz, ±1 in the least significant recorded digit.
c. PPM from internal $C_6F_6$, upfield positive. Estimated accuracy is ±0.05 ppm.

For all entries, the subscript "A" denotes fluorine *trans* to the resonant fluorine of fluorophenoxy group, the subscript "B" an oxygen *trans* to the resonant fluorine or fluorophenoxy group.

approximately five times as great for the tungsten methoxy-fluorides as for the tellurium methoxy-fluorides supports the conclusion that not only does the π interaction occur in the tungsten species as has been previously proposed [5,6,10] but that it is a major contribution to the bonding. This hypothesis is also supported by our study of $ROWF_5$ species [11], in which the axial W-F shift was estimated to be influenced 3.5 times as much by π effects as by σ effects.

TABLE 2

NMR data for $(C_6H_5O)_nWF_{6-n}$ molecules[a]

| Compound | $\delta F_A$ | $\delta F_B$ | $J_{F-F}$[b] |
|---|---|---|---|
| $ArOWF_5$[c] | 39(39,33) | 54(53,47) | 64(65,63) |
| *cis*$(ArO)_2WF_4$ | 78(81,77) | 85(89,84) | 64(68,62) |
| *fac*$(ArO)_3WF_3$ | - | 112(113,-) | - |
| *mer*$(ArO)_3WF_3$ | 100 | 112 | 61 |
| *cis*$(ArO)_4WF_2$ | - | 137 | - |
| $(ArO)_5WF$ | - | 154 | - |

a. $CH_2Cl_2$ solutions except where noted. Chemical shifts in ppm from $WF_6$, upfield positive. Referenced to external $CCl_3F$ with $\delta WF_6 = \delta CCl_3F + 165 \pm 2$ ppm. Values in parentheses are from ref. 5 and 10 respectively. Subscripts A and B as in Table 1.
b. Values in Hz, ± 3.
c. $C_6F_6$ solution, ref. 7.

The detailed chemical shift trends within the $(ArO)_nWF_{6-n}$ series also give a consistent bonding-chemical shift correlation. The overall trend to higher field with increasing phenoxy substitution is evident. Since upfield shifts correspond to more electron density in the fluorine p orbitals (*i.e.* more "ionic" fluorine) a plausible explanation is that the less electronegative oxygens are better π donors to the empty tungsten dπ orbitals than are the fluorines. Consequently fluorine to tungsten donation decreases steadily as more oxygens are added, yielding the observed upfield shifts. The same conclusion regarding the π-bonding ability of oxygen *vs* fluorine has been noted in organic substituent studies [3]. McFarlane *et al.* [10] have similarly analyzed the trends for the methoxy series in

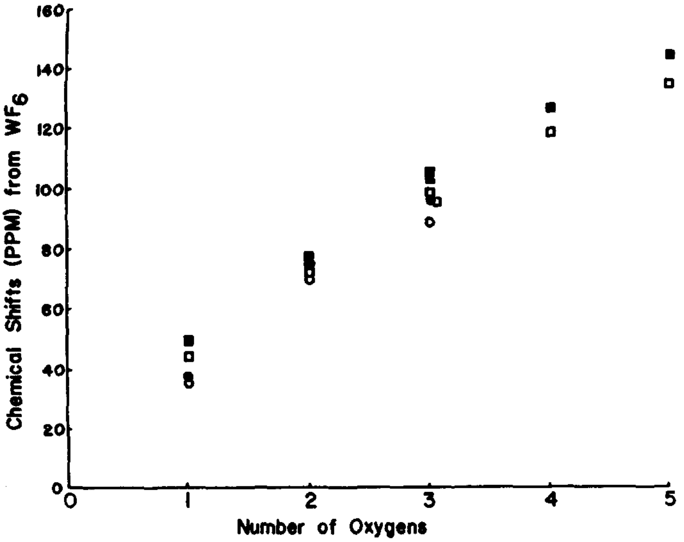

Figure 1. Chemical shifts of W-$\underline{F}$ fluorine nuclei in $(FC_6H_4O)_nWF_{6-n}$ molecules. Solid symbols represent molecules with *para*-fluorophenoxy groups, open symbols *meta*-fluorophenoxy. Squares have oxygen *trans* to the resonant fluorine, circles have fluorine *trans* to the resonant fluorine.

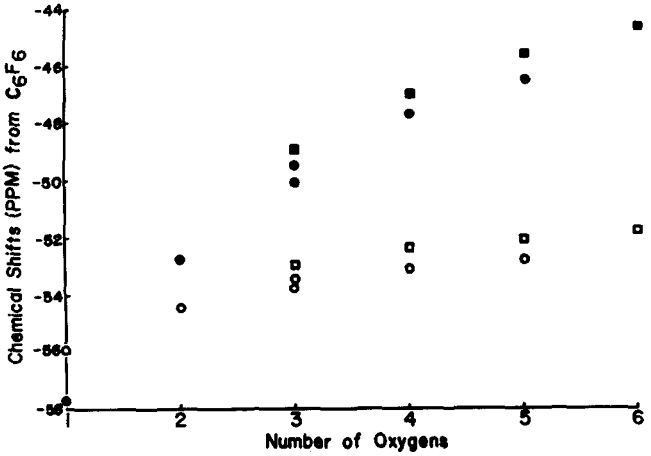

Figure 2. Chemical shifts of aryl fluorine nuclei in $(FC_6H_4O)_nWF_{6-n}$ molecules. Solid symbols represent *para*-fluorophenoxy groups, open symbols *meta*-fluorophenoxy. Squares have oxygen *trans* to the resonant group, circles have fluorine *trans* to the resonant group.

terms of this Gutowsky shift-electronegativity basis. The predicted linear relationship is not realized in either the methoxy series [6,10] or in the present study, as is clear from Figure 1. Instead, the effect of each additional oxygen becomes progressively and regularly smaller. While no unambiguous explanation of this curvature is presently possible, the simple σ-π bonding model provides a ready rationalization. Since all ligands, $RO^-$ or $F^-$, are both σ and π donating to tungsten(VI), there is no opportunity for synergistic metal to ligand back donation. There must, however, be a limit to the capacity of the tungsten orbitals to accept electrons, and if this limit is somewhere between the amount donated by the six fluorines in $WF_6$ and the amount which would be donated by six oxygens similar to the one in $ROWF_5$, then a saturation of the acceptor orbitals will occur. Hence the electron transfer, and the chemical shifts, will be less than a linear function of the number of oxygen atoms.*

Smaller but equally consistent chemical shift effects can also be noted through the series. For any given value of n, the W-F resonance in $(FArO)_nWF_{6-n}$ is invariably at higher field for the *para* substituent than for the *meta*, with the implication that the *para*-fluorophenoxy group is a better π-donor to tungsten than is *meta*-fluorophenoxy. Again, this is consistent with organic substituent studies which indicate that fluorine is a π-donor to the benzene ring and is more effective from the *para* than from the *meta* position. It may also be noted that, for a given degree of substitution, fluorine with an oxygen *trans* to it resonates at higher field than fluorines *trans* to each other. Since *trans* ligands can interact with each other through two dπ oribtals of the metal, while *cis* ligands interact through only one π orbital, the influence of a *trans* oxygen would be expected to be larger. A more detailed and quantitative study of this effect has been reported for the series $(RO)WF_5$ [11].

The shifts in the phenoxy compounds follow exactly the same trends. They are included primarily to provide a complete set of data since only partial sets have heretofore been published [5,10].

## Fluorophenoxy groups

Since both W-F and W-OR linkages can be considered to be electron donors to the tungsten(VI) center, the chemical shift trends of the aryloxy

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* We have begun a study of the influence of the organic substituent, R, on the curvature in an attempt to examine this saturation hypothesis further

fluorines should parallel those of the directly bonded fluorines. This expectation is realized to a remarkable degree, and is readily apparent from a comparison of Figure 2, the Ar-$\underline{F}$ shifts, and Figure $\underline{1}$, the W-$\underline{F}$ shifts. The same general upfield shift with increasing oxy substitution is observed, again due to the presumably greater electron donation from oxygen to tungsten than from fluorine to tungsten. Thus, for $LWF_{5-n}(OR)_n$, whether L is fluorine or fluorophenoxy, as n increases the $WF_{5-n}(OR)_n$ moiety becomes progressively less electron withdrawing from L and thus the chemical shifts of the fluorine nuclei in L move to higher field. Similarly, it is observed that those fluorophenoxy groups *trans* to another fluorophenoxy, *i.e.*, to oxygen, invariably resonate at higher field than those *trans* to fluorine.

Following Taft, *et al.*, the *meta*- and *para*-fluorophenyl chemical shifts have been converted into $\sigma_I$ and $\sigma_R^o$ values [3] and are collected in Table 3. In terms of the original inductive and resonant interpretations,

TABLE 3

Substituent constants, $\sigma_I$ and $\sigma_R^o$, for $(FC_6H_4O)_nWF_{6-n}$ molecules[a]

| Compound | $\sigma_{I(A)}$ | $\sigma_{I(B)}$ | $\sigma^o_{R(A)}$ | $\sigma^o_{R(B)}$ |
|---|---|---|---|---|
| $ArOWF_5$ | .92 | | .05 | |
| *cis*$(ArO)_2WF_4$ | .72 | | -.06 | |
| *fac*$(ArO)_3WF_3$ | .59 | | -.14 | |
| *mer*$(ArO)_3WF_3$ | .63 | .51 | -.13 | -.14 |
| *cis*$(ArO)_4WF_2$ | .53 | .43 | -.18 | -.18 |
| $(ArO)_5WF$ | .49 | .39 | -.22 | -.22 |
| $(ArO)_6W$ | | .34 | | -.24 |

a. Calculated from: $\sigma_I = -0.141\ (\delta meta + 49.28)$ and $\sigma_R^o = -0.0339\ (\delta para - \delta meta)$. Subscript "A" denotes fluorine *trans* to the resonant group, "B" an oxygen *trans* to the resonant group. These σ values may differ slightly from the strict Taft values in that 1) they are referenced to internal $C_6F_6$ solvent rather than $C_6H_5F$, and 2) chemical shifts are for approximately 1 molar solutions. See text for further comments.

the $-OWF_{5-n}(OR)_n$ substituent proceeds smoothly with increasing values of n from a strongly inductive and slightly resonant withdrawing group to a moderately inductive withdrawing and a resonant donating group. The latter is more typical or organic oxy-bound substituents. The values $\sigma_I$ and $\sigma_R^o$ for $(FC_6H_4O)_6W$ are comparable to those for the halogens, and thus suggest that the $-OW(OR)_5$ group would be *ortho-para* directing, and this result has been observed by Mortimer and Strong [12] in the nitration and bromination of $(C_6H_5O)_6W$.

It has been pointed out, however, that the correlation of *meta* shifts with a strictly inductive effect is of doubtful validity and that both *meta* and *para* shifts are functions of the aromatic π-system [13]. While the data in the present work provide no unequivocal basis for assigning the relative improtance of sigma or pi transmittal at either position, they do strongly support the conclusion that the same electronic perturbations are responsible for the W-F shifts, *p*$FC_6H_4$ shifts and the *m*$FC_6H_4$ shifts; and the ease with which these shifts are correlated with a bonding model which involves extensive π-bonding gives little reason to doubt that the *meta* shifts in this series of compounds are also influenced most strongly by perturbations of the π system. The only major differences in the chemical shift parameters for these three different types of fluorine nuclei are the general region in which the resonances are observed (*i.e.* W-F resonates at much lower field than F-Ar) and the magnitude of the chemical shift

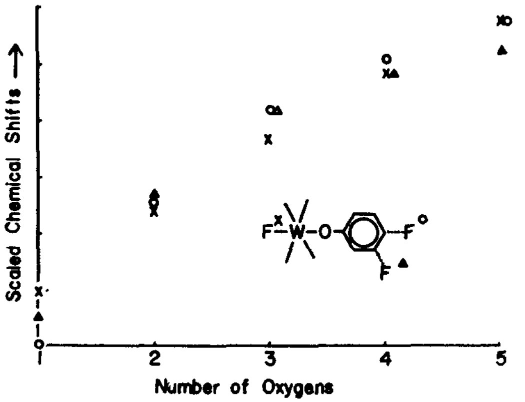

Figure 3. Chemical shifts scaled to illustrate similar trends for WF, *para*-ArF, and *meta*-ArF. Scale factors used are 1, 10, and 30, respectively. The origins are also translated along the ordinate

change from one member of the series to the next. This point can be readily appreciated from the data plotted in Figure 3 where the chemical shifts of W-F, *p*-F and *m*-F are multiplied by 1, 10, and 30, respectively, then translated to bring the data into approximate coincidence. The factor of three differences in sensitivity between *para* and *meta* positions is normal although the point by point correspondence would not be expected in less closely related series. The order of magnitude increase in sensitivity of the directly bound fluorines is remarkable, and should provide a very sensitive test as new theoretical approaches are brought to bear on the problem of calculating chemical shifts in large metal-containing molecular systems. In this connection, we note that Flygare and Goodisman [14] have derived the expression $\sigma_{Av}^{d} = \sigma_{Av}^{d}$ (free atom) $+ \frac{e^2}{3mc^2} \sum_{\alpha}' (Z_\alpha / r_\alpha)$ for the diamagnetic contribution to the shielding, and that the results from this expression are usually in good agreement with more rigorous quantum mechanical calculations where these have been carried out, *i.e.* for small binary fluorides. Mason [15] has recently published an extensive series of $\sigma_{Av}^{d}$ values for binary fluorides assuming the validity of this expression for all species. Some difficulties arise if it is assumed that this approximation to $\sigma_{Av}^{d}$ can be used for the larger molecular systems in this study. The large chemical shifts observed for the W-F fluorine nuclei are particularly useful for comparison with calculated $\sigma_{Av}^{d}$ values, since the differences in measured shifts from one compound to another are considerably larger than would be expected from bulk susceptibility or aromatic anisotropy effects.* Since precise geometrical parameters are not available for the phenoxy tungsten fluorides, we have approximated all W-O and W-F bond lengths as 180 pm, all C-C, C-O, and C-F bond lengths as 140 pm, octahedral coordination about tungsten, and all W-O-C bond angles as 180°. While a value of 155° would probably be more appropriate for the bond angles [16], the assumption of linearity greatly simplifies calculations and will not change the relative order of the results. The value of $\sigma_{Av}^{d}$ (free atom) for fluorine is 471 ppm [17]. With these assumptions we calculate the following diamagnetic contributions to the W-F shieldings: $WF_6$, + 1010 ppm; $(pFC_6H_4O)_5WF$, + 1380 ppm; $pFC_6H_4OWF_5$, + 1070 for the fluorine *trans* to oxygen (axial) and + 1090 for the four fluorines *cis* to

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* The close correspondence between the W-F chemical shifts in the series $(CH_3O)_nWF_{6-n}$ [6], in which there can be no aromatic anisotropy effects, and the present series of aryloxy compounds reinforces the supposition that aromatic anisotropy has relatively little influence on the observed chemical shifts.

oxygen (equatorial). A diamagnetic shielding change of + 370 ppm from $WF_6$ to $(pFC_6H_4O)_5WF$ would require a paramagnetic shielding change of -225 ppm to yield the observed total chemical shift difference of + 144 ppm. A more negative value for $\sigma_{Av}^{p}$, however, is not expected on qualitative grounds, *vide supra*, nor would it be generally expected that changes in the diamagnetic term would dominate the paramagnetic term in the $^{19}F$ shielding of $d^0$ compounds [15]. Similarly, the diamagnetic shielding in $pFC_6H_5OWF_5$ is calculated to be greater for the equatorial fluorine nuclei than for the axial fluorine nucleus, while the measured (total) chemical shifts are invariably at higher field for the axial fluorine than for the equatorial fluorines. Again, the changes in $\sigma_{Av}^{p}$ must both be negative, although less negative for the axial fluorine, -13 ppm, than for the equatorial fluorines -42 ppm. It may be that the assumption that the fluorine chemical shifts in these molecules are dominated by the paramagnetic shielding term, which reflects p orbital occupation [4-7, 10,11], is incorrect, despite the excellent qualitative agreement with the experimental results. Conversely, the Flygare-Goodisman approximation for $\sigma_{Av}^{d}$ may not be sufficiently accurate for these larger (electronically and spatially) molecules. Substantial improvements in *ab initio* calculation techniques will be needed to provide an unambiguous answer.

## EXPERIMENTAL

### Materials and manipulations

Tungsten hexafluoride and the phenols were obtained from commercial sources. The phenols were used as received. Traces of $SiF_4$ were removed from $WF_6$ by trap-to-trap vacuum fractionation. The purified $WF_6$ was stored and measured from a calibrated all metal vacuum line with a Monel Bourdon tube pressure gauge. All manipulations were carried out either in grease-free glass or metal vacuum lines or under a blanket of dry nitrogen.

### Synthesis

The intermediate silyl ethers were prepared from the phenols by standard methods [18] and purified by trap-to-trap vacuum fractionation. The products were characterized by $^1H$ nmr and the expected 4:9 proton ratio verified by integration. The fluoro-aryloxytungsten fluorides were prepared in 5mm O.D., 3.4 mm I.D. nmr tube reactors as previously described [6,11]. Solutions were approximately 1 molar in tungsten. Control of reactant stoichiometry does not lead to a single product in most cases. At least three products were observed in all tubes where the ratio $ArOSiMe_3$ to $WF_6$ was greater than 1:1. This is in contrast to the experience with methoxy substitution, and reflects the tendency toward statistically random substitution as the substituents become more similar [19]. Monosubstitution takes place rapidly at room temperature, but to effect further substitution the tubes were heated behind a safety shield to 100°C for 1 to 2 hours. The extent of overall reaction is easily monitored by noting the intensity of the $Me_3SiF$ doublet in the $^1H$ nmr spectrum. Some crystallization of products took place in the nmr tubes, especially for the *para* isomers. These solids were centrifuged to the top of the tube prior to nmr analysis. Phenoxytungsten fluorides were prepared similarly, but from previously isolated $C_6H_5OWF_5$ and in $CH_2Cl_2$ solution.

## Instrumentation and spectral analysis

Fluorine nmr spectra were recorded on modified commercial instruments operating at 56.4 and 84.7 MHz. All frequencies for the fluorophenoxy species were obtained on the 84.7 MHz instrument and were measured from either the centerband or an appropriate 12.5 KHz sideband of internal $C_6F_6$. Frequencies for the phenoxy compounds were obtained at 56.4 MHz and measured by audio sideband matching with external $CCl_3F$. In most cases, the necessary chemical shifts and coupling constants could be taken directly from the observed spectra. Assignments for the $A_2B_2$ spectra of *cis*$(ArO)_2WF_4$ were verified by computer simulation of the observed spectra using the FREQUINT IV program [20]. Most of the species were observed in more than one sample tube. The data presented in Table 1 are for the tubes with the best signal to noise and resolution.

The chemical shift difference between $C_6F_6$ and $C_6H_5F$ under the conditions of the measurements of the fluorophenoxy species, necessary for the conversion of *meta* shifts to $\sigma_I$ parameters, was established by preparing a tube which contained 1.5 mmoles of *m*$C_6H_4FOSiMe$, 0.5 mmoles of $WF_6$, 0.5 mmoles of $C_6H_5F$, and 0.2 ml of $C_6F_6$. The course of the reaction was monitored by observing the aromatic $^{19}F$ region of the spectrum. From the point when all the $WF_6$ had been at least mono-substituted until the completion of the reaction, the shift of $C_6H_5F$ from $C_6F_6$ was -49.88 ± 0.05 ppm.

During the course of the reaction the species $(mC_6H_4FO)_nWF_{6-n}$, n = 1-4, were clearly observed. Their chemical shifts as measured from internal $C_6H_5F$ and corrected to $C_6F_6$ by subtracting 49.88, and as measured directly from $C_6F_6$, agreed to within ± 0.1 ppm with the values in Table 1. The correction to infinite dilution has been shown to be negligable for similar solutions by Hogben and Graham [20]. We find a chemical shift difference of -48.97 ppm between $C_6F_6$ and $C_6H_5F$ in $CH_2Cl_2$ solution, which suggests that the use of $C_6F_6$ rather than a nonaromatic solvent does not introduce such serious errors as to preclude comparison with other Taft parameters. The $\sigma_I$ values of Table 3, however, may therefore all be shifted by approximately 0.1 σ unit compared to other tabulated values.

## Stereochemical assignments

In most cases, stereochemical assignments of the observed resonances were unambiguous when made from the observed coupling and/or intensities, *viz*, $ArOWF_5$, the aromatic portion of *cis*$(ArO)_2WF_4$, *fac*$(ArO)_3WF_3$, *mer*$(ArO)_3WF_3$, the W-$\underline{F}$ portion of *cis*$(ArO)_4WF_2$, $(ArO)_5WF$, and $(ArO)_6W$. The $W\underline{F}$ resonances of *cis*$(ArO)_2WF_4$ and the aromatic $\underline{F}$ resonances of *cis*$(ArO)_4WF_2$ were assigned to be consistent with the remainder of the data. Partial confirmation of the assignments for *cis*$(ArO)_2WF_4$ was obtained from the pronounced broadening of the upfield half of the $A_2B_2$ spectrum, particularly for the *para*-fluorophenoxy substituents. This presumably results from unresolved coupling between the W-$\underline{F}$ fluorine nuclei and the fluorine nucleus on the *trans* group. The *cis* coupling would be expected to be smaller [6].

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