

## Solvent Induced Variation of *para*-<sup>1</sup>H and *para*-<sup>19</sup>F NMR Chemical Shifts in Polyfluoro-substituted Phenols and Thiols

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<sup>13</sup>C, <sup>1</sup>H, and <sup>19</sup>F chemical shifts of aromatic compounds have with considerable success been predicted from  $\pi$ -electron charge densities and bond orders calculated from MO theory.<sup>1-3</sup> In the special case where these nuclei are situated *para* to a varied substituent, there is theoretical justification for relating the chemical shift to the change of  $\pi$ -electron density at the *para* carbon atom.<sup>4,1</sup> This hypothesis is supported by several experiments. Figey has shown that the *para*-<sup>1</sup>H shift in a series of monosubstituted benzene derivatives, depends linearly on the calculated  $\pi$ -electron density at the adjacent carbon atom.<sup>5</sup> Analogous results have been obtained by Wu<sup>6</sup> and by Schneider<sup>6,7</sup> for the *para* shieldings of <sup>13</sup>C, <sup>1</sup>H, and <sup>19</sup>F in monosubstituted benzenes and fluorobenzenes. The relationship between the *para*-<sup>19</sup>F shift in pentafluorophenyl derivatives and the corresponding <sup>13</sup>C shift in phenyl compounds,<sup>8</sup> indicates that fluorination of the aromatic ring does not alter the functional

dependence between the  $\pi$ -electron density and the <sup>19</sup>F shift, a conclusion being in accordance with calculations performed by Emsley.<sup>9</sup>

From the mentioned correlations, a linear relationship is to be expected between the *para*-<sup>1</sup>H shift of 2,3,5,6-tetrafluorophenyl derivatives and the *para*-<sup>19</sup>F shift of pentafluorophenyl compounds. Instead of testing this hypothesis by measuring <sup>1</sup>H and <sup>19</sup>F chemical shifts in an inert solvent, this work is concerned with the effect of solvent on the *para*-<sup>1</sup>H and *para*-<sup>19</sup>F shifts in two particular compounds; 2,3,5,6-tetrafluorophenol (TFP) and pentafluorophenol (PFP).

Table 1 lists values of  $\delta_p(^1\text{H})$  and  $\delta_p(^{19}\text{F})$ , respectively, for TFP and PFP in solvents of highly differing electron donor ability. Considering the similar environment of the OH substituent, the degree of solvent interaction on this substituent should be nearly of the same magnitude in the two compounds studied. Assuming this interaction to be reflected in  $\delta_p(^1\text{H})$  and  $\delta_p(^{19}\text{F})$ , Table 1 shows that the latter quantity is by far the most sensitive measure of this effect. There is, however, no strong relationship between  $\delta_p(^1\text{H})$  and  $\delta_p(^{19}\text{F})$ , contrary to what is expected from the previously mentioned correlations. This negative result indicates that active centers besides OH are present. As far as PFP is concerned, there is, referring to the inertness of the pentafluorophenyl group, no reason to assume other significant contributions to

Table 1. Chemical shifts (ppm) of the *para* situated nucleus in PFP, TFP, and TTF as function of solvent at room temperature.

Solvent	$\delta_p^{\text{PFP}}(^{19}\text{F})$	$\delta_p^{\text{TFP}}(^1\text{H})$	$\delta_p^{\text{TTF}}(^1\text{H})$	$\delta_p^{\text{TTF}}(^1\text{H}) - \delta_p^{\text{TFP}}(^1\text{H})$
CF <sub>3</sub> COOH	4.788	6.697	6.860	0.163
C <sub>2</sub> Cl <sub>4</sub>	5.750	6.615	6.828	0.213
CCl <sub>4</sub>	5.766	6.643	6.858	0.215
C <sub>2</sub> H <sub>5</sub> Br	6.756	6.681	6.932	0.251
CH <sub>3</sub> NO <sub>2</sub>	7.295	6.795	7.093	0.298
CH <sub>3</sub> CN	8.118	6.752	7.110	0.358
(CH <sub>3</sub> ) <sub>2</sub> CO	8.596	6.870	7.278	0.408
CH <sub>3</sub> OH	9.531	6.668	7.120	0.452

2.0 M solutions. <sup>19</sup>F shifts are upfield from internal C<sub>6</sub>F<sub>5</sub> and <sup>1</sup>H shifts downfield from internal TMS.

$\delta_p(^{19}\text{F})$ -values were calculated by means of computer analysis.

$\delta_p(^1\text{H})$ -values were taken as the position of the center peak.

$\delta_p(^{19}\text{F})$ . Thus if OH-solvent interaction affects  $\delta_p(^1\text{H})$  and  $\delta_p(^{19}\text{F})$  in a parallel way as discussed above, there must be an additional solvent-induced interaction affecting  $\delta_p(^1\text{H})$ . As the direction of the observed  $^1\text{H}$  shift is downfield on increasing the electron donor ability of the solvent, this extra contribution causes a shift in direction opposite to the one induced by perturbation of the OH group. An explanation of the observations can be given in terms of hydrogen bonds between solvent electron donor groups and the aromatic proton. This is not unreasonable as the four aromatic fluorine atoms must be expected to activate the ring proton towards hydrogen bonding.

An attempt at correcting the  $^1\text{H}$  shifts in TFP for the supposed solvent interaction with the *para*-H proton, can be made by subtracting the corresponding values of  $\delta(^1\text{H})$  for 2,3,5,6-tetrafluorothiols (TFT), Table 1. The assumptions which must be fulfilled for taking this difference as a measure of the OH-solvent induced shifts, are:

- SH-solvent interactions are not transmitted to the *para* position.
- The extent to which the *para*-H proton participates in solvent interaction is equal in TFP and TFT.

The validity of (a) is strongly supported by the small variation observed for the *para*- $^{19}\text{F}$  chemical shift in pentafluorothiols on changing the solvent from trifluoroacetic acid to acetonitrile. At room temperature this was found to be less than 0.05 ppm upfield for 2.0 M solutions. Taking into account the greater ability of the OH-oxygen lone pair electrons to be delocalized to the *para* position, one should expect the aromatic proton of TFP to be slightly less acid than the one of TFT. Nevertheless, in the light of the otherwise similar structures of these two compounds (b) is not thought to represent any serious limitation. The linearity obtained between  $\delta_p^{\text{TFP}}(^{19}\text{F})$  and the corrected values of  $\delta_p^{\text{TFT}}(^1\text{H})$ , Fig. 1, strongly indicates that the OH solvent induced variation of the

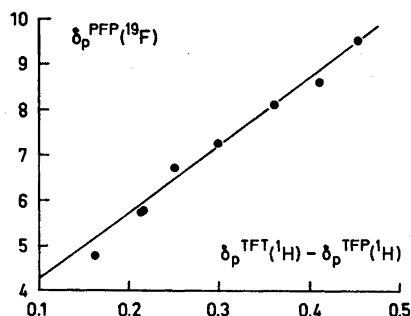


Fig. 1

$\pi$ -electron charge density at the *para*-C atom in TFP can be measured by the difference between the  $\delta_p(^1\text{H})$  values of TFT and TFP. This gives additional evidence for the theory referred to above. The results also illustrate the importance of taking into account the effect of solvent on aromatic protons whenever chemical shifts of such nuclei are considered.

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