

## A Non-stereochemical Approach to Silicon–Nitrogen $\pi$ -Bonding

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A study of pentafluorophenyl derivatives led us recently to suggest<sup>1</sup> that there was a linear relationship between the *ortho-para* fluorine coupling constant ( $J_{2,4}$ ) and the chemical shift of the *para*-fluorine atom ( $\phi_p$ ); and that by means of this relationship, one might assess the  $\pi$ -interaction

between the pentafluorophenyl group and its substituent. Over 70 pentafluorophenyl derivatives have now been studied (Figure), establishing beyond question the empirical validity of this particular coupling constant–chemical shift correlation.<sup>2</sup> These additional results, supported by

correlations with Taft and Hammett parameters, are also in accord with the earlier<sup>1</sup> view that substituents can be identified as  $\pi$ -donors or  $\pi$ -acceptors with respect to the pentafluorophenyl ring in accordance with their position on the graph of  $J_{2,4}$  against  $\phi_p$ , as indicated in the Figure.<sup>2</sup>

We have examined several pentafluoroaniline derivatives with results that are pertinent to the current re-examination of the concept of nitrogen-silicon  $\pi$ -bonding.<sup>3-5</sup> The planarity of trisilylamine (and, presumably, the  $sp^2$  hybridization of the  $\sigma$  bonds of nitrogen) has long been explained

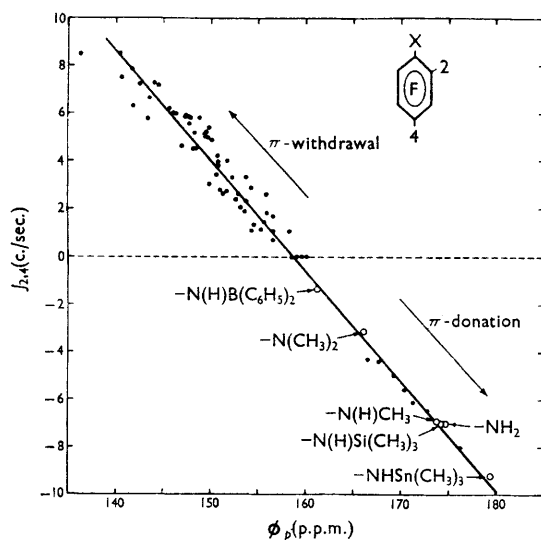


FIGURE. Plot of the ortho-para coupling constant ( $W$ ) against chemical shift of para-fluorine relative to  $\text{CFCl}_3$  ( $\phi_p$ ) for pentafluorophenyl derivatives. Open circles labelled according to the substituent on the pentafluorophenyl ring are discussed in the text. Closed circles are included to demonstrate the linearity of the relationship.

in terms of nitrogen to silicon ( $p \rightarrow d$ )  $\pi$ -bonding. It was assumed by many that this effect on the  $\sigma$ -hybridization and geometry of nitrogen would

be a necessary consequence of ( $p \rightarrow d$ )  $\pi$ -bonding in other silylamines. Thus it was surprising when the value of  $J(^{15}\text{N}-\text{H})$  in  $\text{Ph}^{15}\text{NHSiMe}_3$ , which was expected to increase with increased percentage of  $s$  character in the nitrogen  $\sigma$ -orbitals, was but little changed from values reported for aniline itself.<sup>3</sup> As was pointed out,<sup>4</sup> the non-planar geometry inferred from coupling constant measurements did not exclude the possibility of  $\pi$ -bonding between the lone pair and silicon  $d$ -orbitals, which would be possible even in a pyramidal silylamine. The need for a non-stereochemical means of investigating nitrogen-silicon  $\pi$ -bonding has been stressed;<sup>5</sup> we believe that the approach suggested here may fill this need, since it depends only on the electron distribution as experienced by the pentafluorophenyl ring.

It is evident from the Figure that the  $-\text{NH}_2$  group is a  $\pi$ -donor, the result of interaction of the lone pair with the pentafluorophenyl ring. Replacement of hydrogen by a group capable of  $\pi$ -bonding with nitrogen should reduce donation to the pentafluorophenyl ring. Thus in the compound  $\text{C}_6\text{F}_5\text{NH}\cdot\text{BPh}_2$ , where nitrogen to boron ( $p \rightarrow p$ )  $\pi$ -bonding is expected, donation to the pentafluorophenyl ring is much reduced, as shown in the Figure. Surprisingly, however, substitution of hydrogen by a trimethylsilyl group does not change the  $\pi$ -donation to the ring. From this observation, we conclude that there is no appreciable  $\pi$ -character in the nitrogen-silicon bond in  $N$ -trimethylsilylpentafluoroaniline.

It is also apparent from the Figure that substitution of hydrogen by the trimethyltin group enhances  $\pi$ -donation to the ring; this is in accord with the enhanced basicity of organotin amines.<sup>6</sup>

It is of interest that  $\pi$ -donation by the  $NN$ -dimethylamino-group is less than that by the  $N$ -methylamino- and amino-substituents. This is not unexpected, since previous work<sup>7</sup> has shown that steric interaction between the methyl groups and the *ortho*-fluorines inhibits resonance between the lone pair and the pentafluorophenyl ring.

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<sup>5</sup> E. W. Randall and J. J. Zuckerman, *Chem. Comm.*, 1966, 732.

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