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# A priori calculation of chemical shifts in $^{19}F$ NMR spectroscopy. 4. Testing our model with new experimental values

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**Abstract**

This paper deals with the application of the previously presented model and computer program for predicting $^{19}F$ NMR chemical shifts to a set of essentially new experimental values recently published in this journal.

*Keywords:* NMR spectroscopy; A priori calculations; Model testing

## 1. Introduction

We have already presented in this journal [1] a calculation model intended to predict $^{19}F$ NMR chemical shifts for saturated hydrohalogenated fluorocarbon. This model was improved and extended to carboxylic acids [2], and, finally, a computer program was established in order to help with the calculation [3]. This calculation takes into account the paramagnetic effect of substituents up to five bonds removed from the considered fluorine nucleus and a diamagnetic term related to the actual charge on the fluorine atom. In a recent paper, Weigert [4] published a set of 99 $^{19}F$ chemical shifts in saturated chlorofluoropropanes. Some of them concern the same nuclei (76 different nuclei were studied). Most of them have not been published previously.

We believe that these new data give us an outstanding opportunity to test our model and program.

## 2. Results

The chemical shifts of each nucleus have been calculated using our program, the diamagnetic term being $2\times10^{-6}$. Table 1 lists the experimental and calculated values of the chemical shifts in $10^{-6}$ and also the differences, i.e. calculated minus experimental shifts. The nuclei are numbered in the first column. The chemical shifts for nuclei 23 and 24 have already been published [5] and are not very different from Weigert's values: 66.5 and 112.3 instead of 68.0 and 113.8 respectively (even if Weigert's values are both higher). In Fig. 1 the calculated shifts are plotted vs. experimental values together with the identity line representing the ideal correlation.

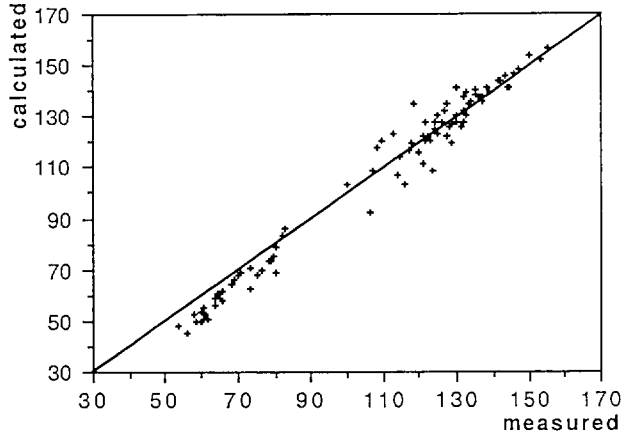


Fig. 1. Comparison between experimental chemical shifts and values calculated using a previously published computer program [3]. All shift data are quoted in $10^{-6}$.

## 3. Discussion

As one can see from Fig. 1, the prediction given by our model is, on the whole, quite good, despite a slight

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Table 1
Comparison between the experimental and calculated $^{19}F$ chemical shifts (in $10^{-6}$)

| Nucleus No. | Compound | Experimental shift | Calculated shift | Difference [a] |
|---|---|---|---|---|
| 1 | $CCl_3CCl_2\mathit{C}FHCl$ | 126.6 | 132.1 | +5.5 |
| 2 | $CCl_3\mathit{C}FClCHCl_2$ | 100.2 | 103.5 | +3.3 |
| 3 | $\mathit{C}FCl_2CCl_2CHCl_2$ | 53.8 | 48.0 | −5.8 |
| 4 | $CCl_3\mathit{C}FClCFHCl$ | 121.9 | 120.1 | −1.8 |
| 5 | $CCl_3CFCl\mathit{C}FHCl$ | 137.2 | 137.9 | +0.7 |
| 5 | $CCl_3CFCl\mathit{C}FHCl$ | 135.6 | 137.9 | +2.3 |
| 6 | $CCl_3\mathit{C}FClCFHCl$ | 109.5 | 120.1 | +10.6 * |
| 7 | $\mathit{C}F_2ClCCl_2CHCl_2$ | 55.9 | 45.4 | −10.5 * |
| 8 | $CCl_3CCl_2\mathit{C}F_2H$ | 117.2 | 116.5 | −0.7 |
| 9 | $\mathit{C}FCl_2CCl_2CFHCl$ | 57.8 | 52.7 | −5.1 |
| 10 | $CFCl_2CCl_2\mathit{C}FHCl$ | 131.7 | 137.7 | +6.0 |
| 11 | $\mathit{C}FCl_2CFClCCHCl_2$ | 60.0 | 53.8 | −6.2 |
| 12 | $CFCl_2\mathit{C}FClCHCl_2$ | 108.5 | 117.8 | +9.3 * |
| 13 | $CCl_3\mathit{C}F_2CHCl_2$ | 106.5 | 92.2 | −14.3 * |
| 14 | $CF_2ClCCl_2\mathit{C}FHCl$ | 133.9 | 135.5 | +1.6 |
| 15 | $\mathit{C}F_2ClCCl_2CFHCl$ | 58.6 | 50.1 | −8.5 * |
| 15 | $\mathit{C}F_2ClCCl_2CFHCl$ | 59.7 | 50.1 | −9.6 * |
| 16 | $\mathit{C}F_2ClCFClCHCl_2$ | 61.7 | 51.2 | −10.5 * |
| 16 | $\mathit{C}F_2ClCFClCHCl_2$ | 60.8 | 51.2 | −9.6 * |
| 17 | $CF_2Cl\mathit{C}FClCHCl_2$ | 114.9 | 114.1 | −0.8 |
| 18 | $CCl_3CFCl\mathit{C}F_2H$ | 127.3 | 122.3 | −5.0 |
| 18 | $CCl_3CFCl\mathit{C}F_2H$ | 121.3 | 122.3 | +1.0 |
| 19 | $CCl_3\mathit{C}FClCF_2H$ | 121.7 | 127.1 | +5.4 |
| 20 | $\mathit{C}F_3CCl_2CHCl_2$ | 73.1 | 62.8 | −10.3 * |
| 21 | $CFCl_2CCl_2\mathit{C}F_2H$ | 120.7 | 122.1 | +1.4 |
| 22 | $\mathit{C}FCl_2CCl_2CF_2H$ | 60.4 | 54.9 | −5.5 |
| 23 | $\mathit{C}FCl_2CF_2CCl_2H$ | 68.0 | 64.0 | −4.0 |
| 24 | $CFCl_2\mathit{C}F_2CCl_2H$ | 113.8 | 106.5 | −7.3 |
| 25 | $\mathit{C}FCl_2CFClCFHCl$ | 65.3 | 58.5 | −6.8 |
| 26 | $CFCl_2\mathit{C}FClCFHCl$ | 118.2 | 134.4 | +16.2 * |
| 27 | $CFCl_2CFCl\mathit{C}FHCl$ | 142.1 | 143.5 | +1.4 |
| 26 | $CFCl_2\mathit{C}FClCFHCl$ | 127.2 | 134.4 | +7.2 |
| 25 | $\mathit{C}FCl_2CFClCFHCl$ | 63.5 | 58.5 | −5.0 |
| 27 | $CFCl_2CFCl\mathit{C}FHCl$ | 141.5 | 143.5 | +2.0 |
| 28 | $CCl_3\mathit{C}F_2CFHCl$ | 123.6 | 108.8 | −14.8 * |
| 29 | $CCl_3CF_2\mathit{C}FHCl$ | 147.0 | 148.1 | +1.1 |
| 28 | $CCl_3\mathit{C}F_2CFHCl$ | 107.0 | 108.8 | +1.8 |
| 30 | $\mathit{C}F_2ClCCl_2CF_2H$ | 61.1 | 52.3 | −8.8 |
| 31 | $CF_2ClCCl_2\mathit{C}F_2H$ | 123.0 | 119.9 | −3.1 |
| 32 | $\mathit{C}F_2ClCF_2CHCl_2$ | 65.8 | 61.4 | −4.4 |
| 33 | $CF_2Cl\mathit{C}F_2CHCl_2$ | 115.9 | 102.8 | −13.1 * |
| 34 | $CF_2ClCFCl\mathit{C}FHCl$ | 144.2 | 141.3 | −2.9 |
| 35 | $\mathit{C}F_2ClCFClCFHCl$ | 63.7 | 55.9 | −7.8 |
| 34 | $CF_2ClCFCl\mathit{C}FHCl$ | 144.7 | 141.3 | −3.4 |
| 36 | $CF_2Cl\mathit{C}FClCFHCl$ | 132.5 | 130.7 | −1.8 |
| 35 | $\mathit{C}F_2ClCFClCFHCl$ | 63.9 | 55.9 | −8.0 |
| 36 | $CF_2Cl\mathit{C}FClCFHCl$ | 125.0 | 130.7 | +5.7 |
| 35 | $\mathit{C}F_2ClCFClCFHCl$ | 64.0 | 55.9 | −8.1 |
| 35 | $\mathit{C}F_2ClCFClCFHCl$ | 64.0 | 55.9 | −8.1 |
| 37 | $\mathit{C}F_3CCl_2CFHCl$ | 75.2 | 67.5 | −7.7 |
| 38 | $CF_3CCl_2\mathit{C}FHCl$ | 135.3 | 140.5 | +5.2 |
| 39 | $CF_3\mathit{C}FClCHCl_2$ | 122.3 | 122.4 | +0.1 |
| 40 | $\mathit{C}F_3CFClCHCl_2$ | 80.5 | 68.6 | −11.9 * |
| 41 | $CFCl_2CF_2\mathit{C}FHCl$ | 150.4 | 153.7 | +3.3 |
| 42 | $CFCl_2\mathit{C}F_2CFHCl$ | 124.6 | 123.1 | −1.5 |
| 42 | $CFCl_2\mathit{C}F_2CFHCl$ | 112.5 | 123.1 | +10.6 * |
| 43 | $\mathit{C}FCl_2CF_2CFHCl$ | 70.9 | 68.7 | −2.2 |
| 44 | $\mathit{C}FCl_2CFClCF_2H$ | 64.1 | 60.7 | −3.4 |
| 45 | $CFCl_2CFCl\mathit{C}F_2H$ | 126.0 | 127.9 | +1.9 |
| 46 | $CFCl_2\mathit{C}FClCF_2H$ | 129.6 | 141.4 | +11.8 * |

(continued)

Table 1 (*continued*)

| Nucleus No. | Compound | Experimental shift | Calculated shift | Difference [a] |
|---|---|---|---|---|
| 45 | $CFCl_2CFClCF_2H$ | 129.2 | 127.9 | −1.7 |
| 47 | $CCl_3CF_2CHF_2$ | 120.0 | 115.8 | −4.2 |
| 48 | $CCl_3CF_2CF_2H$ | 131.8 | 132.5 | +0.7 |
| 49 | $CF_2ClCF_2CFHCl$ | 69.0 | 66.1 | −2.9 |
| 50 | $CF_2ClCF_2CFHCl$ | 128.7 | 119.4 | −9.3* |
| 50 | $CF_2ClCF_2CFHCl$ | 118.0 | 119.4 | +1.4 |
| 51 | $CF_2ClCF_2CFHCl$ | 153.6 | 151.5 | −2.1 |
| 52 | $CF_2ClCFClCF_2H$ | 136.0 | 137.7 | +1.7 |
| 53 | $CF_2ClCFClCF_2H$ | 128.3 | 125.7 | −2.6 |
| 53 | $CF_2ClCFClCF_2H$ | 131.3 | 125.7 | −5.6 |
| 54 | $CF_2ClCFClCF_2H$ | 65.9 | 58.1 | −7.8 |
| 54 | $CF_2ClCFClCF_2H$ | 65.5 | 58.1 | −7.4 |
| 55 | $CFCl_2CF_2CF_2H$ | 134.9 | 138.1 | +3.2 |
| 56 | $CFCl_2CF_2CF_2H$ | 73.4 | 70.9 | −2.5 |
| 57 | $CFCl_2CF_2CF_2H$ | 124.7 | 130.1 | +5.4 |
| 58 | $CF_3CCl_2CF_2H$ | 76.2 | 69.7 | −6.5 |
| 59 | $CF_3CCl_2CF_2H$ | 124.5 | 124.9 | +0.4 |
| 60 | $CF_3CF_2CCl_2H$ | 80.0 | 78.8 | −1.2 |
| 61 | $CF_3CF_2CCl_2H$ | 121.1 | 111.1 | −10.0* |
| 62 | $CF_3CFClCFHCl$ | 79.2 | 73.3 | −5.9 |
| 63 | $CF_3CFClCFHCl$ | 138.7 | 139.0 | +0.3 |
| 64 | $CF_3CFClCFHCl$ | 145.7 | 146.3 | +0.6 |
| 63 | $CF_3CFClCFHCl$ | 132.5 | 139.0 | +6.5 |
| 62 | $CF_3CFClCFHCl$ | 78.2 | 73.3 | −4.9 |
| 64 | $CF_3CFClCFHCl$ | 146.0 | 146.3 | +0.3 |
| 65 | $CF_2ClCF_2CF_2H$ | 70.4 | 68.3 | −2.1 |
| 66 | $CF_2ClCF_2CF_2H$ | 128.8 | 126.4 | −2.4 |
| 67 | $CF_2ClCF_2CF_2H$ | 136.8 | 135.9 | −0.9 |
| 68 | $CF_3CF_2CFHCl$ | 155.3 | 156.5 | +1.2 |
| 69 | $CF_3CF_2CFHCl$ | 82.0 | 83.5 | +1.5 |
| 70 | $CF_3CF_2CFHCl$ | 124.0 | 127.7 | +3.7 |
| 70 | $CF_3CF_2CFHCl$ | 132.0 | 127.7 | −4.3 |
| 71 | $CF_3CFClCF_2H$ | 79.5 | 75.5 | −4.0 |
| 72 | $CF_3CFClCF_2H$ | 143.2 | 146.0 | +2.8 |
| 73 | $CF_3CFClCF_2H$ | 130.0 | 130.7 | +0.7 |
| 73 | $CF_3CFClCF_2H$ | 132.6 | 130.7 | −1.9 |
| 74 | $CF_3CF_2CF_2H$ | 82.7 | 85.7 | +3.0 |
| 75 | $CF_3CF_2CF_2H$ | 133.0 | 134.7 | +1.7 |
| 76 | $CF_3CF_2CF_2H$ | 137.9 | 140.9 | +3.0 |

[a] Nuclei exhibiting the most significant difference values are indicated by an asterisk.

tendency towards underestimation especially for the lowest chemical shift values.

The question arises as to which differences are significant. Since some of the measurements listed in Table 1 were repeated, it is possible to answer this question if it is assumed that the overall variance is independent of the value of the chemical shift. This was found to be equal to 18.4 with 23 degrees of freedom. The corresponding confidence interval with a 95% probability is then $8.9\times10^{-6}$. Differences which are less than this value are not significant at this probability level. The nuclei corresponding to the greater difference are indicated by an asterisk in Table 1. In total, 16 nuclei are concerned (21% of the total), but for nuclei 15, 26, 28, 42 and 50, for which two values of the chemical shift are available, one of them enters the confidence interval. On this basis, differences between the experimental and calculated shifts are only significant for 11 nuclei (15% of the total). Moreover, none of the observed differences is greater than $15\times10^{-6}$.

## 4. Conclusions

Our empirical model when compared with the 99 experimental shifts measured by Weigert for 76 different $^{19}F$ nuclei in various chlorofluoropropanes is capable

of predicting 85% of them, taking into account experimental error. Among these, some misassignments of peaks corresponding to minor components may also occur. The calculated shifts generally underestimate the experimental values and the question arises as to whether a general shift should be made of Weigert's values compared with those used to determine the increments of the model. Finally, Weigert's study confirms that $^{19}F$ chemical shifts are largely dependent on distant substituents (see Table 3 in Ref. [4]).

## References

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