

fectively for correct understanding of atomic and molecular orbitals. Figures 2 and 3 are examples of this combination of drawings, where seven 4f atomic orbitals of hydrogen are shown.

$$\psi_{4f_{5z^3-3zr^2}} = (1/3072\sqrt{5\pi}) \exp(-r/4)z(5z^2 - 3r^2)$$

$$\psi_{4f_{3xz^2-r^2}} = (1/1024\sqrt{30\pi}) \exp(-r/4)x(5z^2 - r^2)$$

$$\psi_{4f_{5yz^2-yr^2}} = (1/1024\sqrt{30\pi}) \exp(-r/4)y(5z^2 - r^2)$$

$$\psi_{4f_{3x^2-y^2}} = (1/1024\sqrt{3\pi}) \exp(-r/4)z(x^2 - y^2)$$

$$\psi_{4f_{xyz}} = (1/512\sqrt{3\pi}) \exp(-r/4)xyz$$

$$\psi_{4f_{z^3-3xy^2}} = (1/3072\sqrt{2\pi}) \exp(-r/4)x(x^2 - 3y^2)$$

$$\psi_{4f_{y^3-3yx^2}} = (1/3072/\sqrt{2\pi}) \exp(-r/4)y(y^2 - 3x^2)$$

## Acknowledgment

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# A Short Set of <sup>13</sup>C-NMR Correlation Tables

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Many student textbooks in discussion of <sup>13</sup>C-NMR spectroscopy stress the great value of the method that results from the sensitivity of the chemical shift value to subtle alterations in environment of the individual <sup>13</sup>C nuclei giving the familiar wide spread of resonance of over 200 ppm. This is usually followed by a short discussion of the relationship between  $\delta$  values and (1) mode of hybridization, (2) inductive effects, (3) mesomeric effect and then by provision of tables giving broad ranges of values for <sup>13</sup>C atoms in various environments. The tables are of limited value for structural assignments, allowing unambiguous assignments of signals to be made only for fairly simple molecules having each nucleus in a very different environment from the others. On the other hand, there are a large number of specialist textbooks and original papers that have very detailed sets of correlation tables. Here different sets of additivity constants are defined and used to calculate the chemical shift of a given nucleus by reference to the compound type, the proximity of different functional groups, and by taking into account a number of steric effects. Attempts to refine these calculations lead to the development of more sets of additivity constants and different correction factors applicable to more closely defined chemical systems. This results in a need for a very large number of tables of constants and correction factors, so that the whole operation becomes unwieldy and unmanageable in the context of undergraduate tutorial work. Student texts therefore pay less attention to <sup>13</sup>C spectroscopy than <sup>1</sup>H-NMR spectroscopy. An exception to this is the excellent Open University text in "The Nature of Chemistry, S304," course where, since the spectra are usually less complicated than proton spectra, magnetic resonance spectroscopy is introduced by treating proton decoupled <sup>13</sup>C-NMR spectroscopy. However, the space devoted to the calculation of  $\delta$  values is necessarily limited and as two different bases for calculation are described this treatment can cause confusion to students.

Second-year chemistry students at the University of Bath are given the following set of correlation charts during a nine-hour introductory course on NMR spectroscopy. The students have usually mastered the use of these tables after solving one or two problems and discussing the solutions in

a 1-hr tutorial session. The charts are of particular use to undergraduates in their final-year research projects and to new postgraduates from other university departments. The object of these tables is to enable a student to calculate rapidly approximate  $\delta$  values for <sup>13</sup>C nuclei in as wide a variety of compounds as possible. If the agreement with measured values is within 2-3 ppm, then the author regards this as very satisfactory. Wider deviations are generally due to the author's approximations of published additivity rules. The more crowded is the observed carbon nucleus and the more closely are placed the functional groups, the less good is the agreement with the observed value.

Most of the credit for the contents of this article must go to the authors of "Tabellen zur Strukturaufklärung Organischer Verbindungen mit Spektroskopischen Methoden" (1) and "<sup>13</sup>C-NMR Spektroskopie in der Organischen Chemie" (2) and to those cited in these books. Tables not derived from the above texts have been constructed from the data contained in the splendid microfiche catalog entitled "Carbon-13 NMR Spectral Data" (3) from which  $\delta$  values are taken where possible from spectra determined in CDCl<sub>3</sub> using TMS as internal standard.

## Alkanes and Substituted Alkanes

The  $\delta$  value of a carbon atom <sup>i</sup>C can be calculated as the sum of a series of constants so that

$$\delta = -2.3 + A + B$$

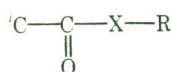
where *A* is the sum of the increments allowed for various substituents depending on their positions as  $\alpha$ ,  $\beta$ , or  $\gamma$  to the <sup>13</sup>C atom in question, *B* is the sum of the branching corrections and -2.3 is the  $\delta$  value for methane. Increments for *A* are given in Table 1; those for *B* in Table 2. The following should be noted in using Table 2.

- 1) The functional groups shown may, for the purpose of selecting the steric correction increment, be regarded as corresponding to the types of carbon atom cited.
- 2) In selecting the increment for the *B* term, for amines and ethers, regard the heteroatom as a carbon atom.

**Table 1. Increments for A, the Shielding Term for Alkanes and Substituted Alkanes (1)**

| Substituent                    | Increments |         |          | Substituent       | Increments |         |          |
|--------------------------------|------------|---------|----------|-------------------|------------|---------|----------|
|                                | $\alpha$   | $\beta$ | $\gamma$ |                   | $\alpha$   | $\beta$ | $\gamma$ |
| —C.sp <sup>3</sup>             | 9.1        | 9.4     | -2.5     | —N<               | 28.3       | 11.3    | -5.1     |
| —C≡C—                          | 4.4        | 5.6     | -3.4     | —N≡               | 30.7       | 5.4     | -7.2     |
| —C=C—                          | 19.5       | 6.9     | -2.1     | —NO <sub>2</sub>  | 61.6       | 3.1     | -4.6     |
| —C <sub>6</sub> H <sub>5</sub> | 22.1       | 9.3     | -2.6     | —S—               | 10.6       | 11.4    | -3.6     |
| —Cl                            | 31.0       | 10.0    | -5.1     | —CHO              | 29.9       | -0.6    | -2.7     |
| —F                             | 70.1       | 7.8     | -6.8     | —CO—              | 22.5       | 3.0     | -3.0     |
| —Br                            | 18.9       | 11.0    | -3.8     | —COOH             | 20.1       | 2.0     | -2.8     |
| —I                             | -7.2       | 10.9    | -1.5     | —COO <sup>-</sup> | 24.5       | 3.5     | -2.5     |
| $\sqrt{\text{O}}$              | 21.4       | 2.8     | -2.5     | —COO—             | 22.6       | 2.0     | -2.8     |
| —O—                            | 49.0       | 10.1    | -6.2     | —CON<             | 22.0       | 2.6     | -3.2     |
| —O—CO—                         | 56.5       | 6.5     | -6.0     | —CN               | 3.1        | 2.4     | -3.3     |

3) O and N-alkyl groups in esters and amides are counted as  $\gamma$ -substituents in calculating the value of A for



The above points are illustrated by the following calculations.

$$\begin{aligned} (1) \text{CH}_3\text{CH}_2^i\text{CH}(\text{OH})\text{CH}_3 & \quad \delta^i = -2.3 + A + B \\ & = -2.3 + (2\alpha^1 + \alpha^2 \\ & \quad + \beta + \gamma) + B \\ & = -2.3 + (9.1 \times 2 + 49.0 + 9.4 \\ & \quad + 0.0) + (-3.7) \\ & = 70.6 \text{ (observed 68.8)} \end{aligned}$$

$$\begin{aligned} (2) \text{CH}_3^i\text{CH}_2\text{CH}(\text{OH})\text{CH}_3 & \quad \delta^i = -2.3 + (9.1 \times 2 + 9.4 \\ & \quad + 10.1 + 0.0) + (-2.5) \\ & = 32.9 \text{ (observed 32.3)} \end{aligned}$$

$$\begin{aligned} (3) (\text{CH}_2\text{OH})_3^i\text{CNO}_2 & \quad \delta^i = 2.3 + (9.1 \times 3 + 61.6 \\ & \quad + 30.3 + 0.0) \\ & \quad + (-8.4 \times 3 - 1.5) \\ & = 90.2 \text{ (observed 94.9)} \end{aligned}$$

$$\begin{aligned} (4) (\text{CH}_3)_3^i\text{CCOCH}_3 & \quad \delta^i = -2.3 + (9.1 \times 3 + 22.5 \\ & \quad + 9.4 + 0.0) + (-15.0) \\ & = 41.9 \text{ (observed 44.3)} \end{aligned}$$

$$\begin{aligned} (5) \text{CH}_3\text{CCH}_2^i\text{CH}_2\text{C}(\text{O})\text{OCH}_2\text{CH}_3 & \quad \delta^i = -2.3 + (9.1 + 22.6 \\ & \quad + 3.0 - 2.5 - 2.5) \\ & = 27.4 \text{ (observed 27.8)} \end{aligned}$$

$$\begin{aligned} (6) \text{CH}_3^i\text{CH}(\text{OCH}_3)\text{CH}_2\text{CH}_3 & \quad \delta^i = -2.3 + (9.1 \times 2 + 49.0 \\ & \quad + 18.8) + (-3.7 \times 2) \\ & = 76.7 \text{ (observed 77.0)} \end{aligned}$$

### Alkenes and Alkene Derivatives

The  $\delta$  value of a carbon atom <sup>i</sup>C can be calculated as the sum of a series of constants such that

$$\delta^i = 122.8 + A + B$$

where A is the sum of the increments allowed for alkyl-substituents  $\alpha$ ,  $\beta$ , and  $\gamma$  to <sup>i</sup>C, B is the correction term for the type of disubstitution and 122.8 is the observed  $\delta$  value for ethene. The increments for A and B are given in Tables 3 and 4. An example of the application of Table 3 is

$$\begin{aligned} (\text{E})-\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3 & \quad \delta^i = 122.8 + A + B \\ & = 122.8 + (\alpha + \beta + \alpha') \\ & = 122.8 + (10.6 + 7.2 - 7.9) \\ & = 132.7 \text{ (observed 132.7)} \end{aligned}$$

**Table 2. Increments for B, the Branching or Steric Correction Term for Alkanes and Substituted Alkanes (4)**

| <sup>13</sup> C atom observed | The number of substituents (other than H) on the $\alpha$ -substituents.        |      |       |       |
|-------------------------------|---|------|-------|-------|
|                               | 1   | 2    | 3     | 4     |
| primary                       | ...   | ...  | -1.1  | -3.4  |
| secondary                     | ...   | ...  | -2.5  | -7.2  |
| tertiary                      | ...   | -3.7 | -9.5  | -15.0 |
| quaternary                    | -1.5  | -8.4 | -15.0 | -25.0 |
| Carbon equivalent             | Functional group  |      |       |       |
| primary                       | —CO <sub>2</sub> H, —CO <sub>2</sub> R, —NO <sub>2</sub>                        |      |       |       |
| secondary                     | —C <sub>6</sub> H <sub>5</sub> , —CHO, —CONH <sub>2</sub> , —CH <sub>2</sub> X* |      |       |       |
| tertiary                      | —COR  |      |       |       |

\* X = OH, —NH<sub>2</sub>, —SH or halogen.

**Table 3. Increments for A and B for the General Alkene Structure (5) —C<sub>β</sub>—C<sub>α</sub>—<sup>i</sup>C=C—C<sub>α'</sub>—C<sub>β'</sub>**

| Position of substitution | Increments A | Type of disubstitution | Increments B |
|--------------------------|--------------|------------------------|--------------|
| $\alpha$                 | 10.6         | $\alpha, \alpha'$ cis  | -1.1         |
| $\beta$                  | 7.2          | $\alpha, \alpha'$ gem  | -4.8         |
| $\gamma$                 | -1.5         | $\alpha', \alpha'$ gem | +2.5         |
| $\alpha'$                | -7.9         | $\beta, \beta'$ gem    | -2.3         |
| $\beta'$                 | -1.8         |                        |              |
| $\gamma'$                | +1.5         |                        |              |

**Table 4. Increments for A for the General Alkene Derivative Structure (1, 6) X—CH( $\alpha$ )=CH<sub>2</sub>( $\beta$ )**

| Substituent X       | Increments |         | Substituent                        | Increments |         |
|---------------------|------------|---------|------------------------------------|------------|---------|
|                     | $\alpha$   | $\beta$ |                                    | $\alpha$   | $\beta$ |
| —Cl                 | 3.3        | -5.6    | —CH <sub>2</sub> Y*                | 12         | -5      |
| —NCOR <sub>2</sub>  | 7.2        | -28.5   | —CH <sub>2</sub> CO <sub>2</sub> H | 6.9        | -4.6    |
| —NO <sub>2</sub>    | 22.8       | -0.4    | —CH <sub>2</sub> CN                | 5.9        | -2.1    |
| —N≡                 | 18.9       | -26.2   | —C <sub>6</sub> H <sub>5</sub>     | 13.0       | -10.5   |
| —OCH <sub>3</sub>   | 31.0       | -38.2   | —C≡N                               | -15.6      | 15.1    |
| —OCOCH <sub>3</sub> | 18.9       | -26.4   | —CO <sub>2</sub> R                 | 6.0        | 8.0     |
| —CH <sub>3</sub>    | 13.4       | -6.9    | —COCH <sub>3</sub>                 | 14.9       | 6.7     |
| —t-Bu               | 26.9       | -13.0   | —CHO                               | 15.8       | 14.8    |
|                     |            |         | —CON<                              | 9.6        | 3.1     |

\* Y = an electronegative atom or group

For Table 4, two examples are

$$\begin{aligned} \text{CH}_2=\text{C}(\text{CH}_3)\text{CONH}_2 & \quad \delta^i = 122.8 + A + B = 122.8 \\ & \quad + (\alpha + \alpha) + B \\ & = 122.8 + (13.4 + 9.6) + (-4.8) \\ & = 141.0 \text{ (observed 139.2)} \\ (\text{E})-\text{CH}_3\text{CH}=\text{CHCOOEt} & \quad \delta^i = 122.8 + \alpha + \beta \\ & = 122.8 + (13.4 + 8.0) + (0.0) \\ & = 144.2 \text{ (observed 144.0)} \end{aligned}$$

Note that <sup>i</sup>C in the part-structure (Z)—R—CH=CH—<sup>i</sup>C< is shielded by between 4 and 9 ppm.

### Alkynes

The  $\delta$  value of a carbon atom <sup>i</sup>C can be calculated as the sum of a series of constants such that

$$\delta^i = 71.9 + A$$

where 71.9 is the  $\delta$  value for ethyne. Increments in A are given in Table 5 and two sample calculations are

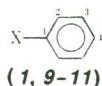
$$\begin{aligned} \text{Bu}^i\text{C}\equiv\text{CCOCH}_3 & \quad \delta^i = 71.9 + (\alpha + \beta + \alpha') \\ & = 71.9 + (6.9 + 4.8 + 4.0) \\ & = 87.6 \text{ (observed 87.0)} \\ p\text{-ClC}_6\text{H}_4\text{—}^i\text{C}\equiv\text{C—CH}_3 & \quad \delta^i = 71.9 + (12.7 - 5.7) \\ & = 78.9 \text{ (observed 79.6)} \end{aligned}$$

**Table 5. Increments for A for the General Structure (8)**

$$-C_{\beta}-C_{\alpha}-C \equiv C-C_{\alpha'}-C-\beta'$$

| Substituents                   | Increments |           |         |          |
|--------------------------------|------------|-----------|---------|----------|
|                                | $\alpha$   | $\alpha'$ | $\beta$ | $\beta'$ |
| -C.sp <sup>3</sup>             | 6.9        | -5.7      | 4.8     | 2.3      |
| -CH <sub>2</sub> OH            | 11.1       | 1.9       |         |          |
| -COCH <sub>3</sub>             | 31.4       | 4.0       |         |          |
| -C <sub>6</sub> H <sub>5</sub> | 12.7       | 6.4       |         |          |
| -CH=CH <sub>2</sub>            | 10.0       | 11.0      |         |          |

**Table 6. Increments for A for the General Structure**



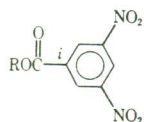
| Substituent X                     | Increments     |                |                |                |
|-----------------------------------|----------------|----------------|----------------|----------------|
|                                   | A <sub>1</sub> | A <sub>2</sub> | A <sub>3</sub> | A <sub>4</sub> |
| -CH <sub>3</sub>                  | 9.3            | 0.8            | 0.0            | -2.9           |
| -Et                               | 15.8           | -0.4           | -0.1           | -2.6           |
| -i-Pr                             | 20.3           | -1.9           | 0.1            | -2.4           |
| t-Bu                              | 22.4           | -3.1           | -0.2           | -2.9           |
| -CH=CH <sub>2</sub>               | 7.6            | -1.8           | -1.8           | -3.5           |
| -C≡CH                             | -6.1           | 3.8            | 0.4            | -0.2           |
| -C <sub>6</sub> H <sub>5</sub>    | 13.0           | -1.1           | 0.5            | -1.0           |
| -CHO                              | 8.6            | 1.3            | 0.6            | 5.5            |
| -COCH <sub>3</sub>                | 9.1            | 0.1            | 0.0            | 4.2            |
| -CO <sub>2</sub> H                | 2.1            | 1.5            | 0.0            | 5.1            |
| -CO <sub>2</sub> <sup>-</sup>     | 7.6            | 0.8            | 0.0            | 2.8            |
| -CO <sub>2</sub> R                | 2.1            | 1.2            | 0.0            | 4.4            |
| -CONH <sub>2</sub>                | 5.4            | -0.3           | -0.9           | 5.0            |
| -CN                               | -15.4          | 3.6            | 0.6            | 3.9            |
| -Cl                               | 6.2            | 0.4            | 1.3            | -1.9           |
| -OH                               | 26.9           | -12.7          | 1.4            | -7.3           |
| -OCH <sub>3</sub>                 | 31.4           | -14.4          | 1.0            | -7.7           |
| -OC <sub>6</sub> H <sub>5</sub>   | 29.1           | -9.5           | 0.3            | -5.3           |
| -OCOCH <sub>3</sub>               | 23.0           | -6.4           | 1.3            | -2.3           |
| -NH <sub>2</sub>                  | 18.7           | -12.4          | 1.3            | -9.5           |
| -N(CH <sub>3</sub> ) <sub>2</sub> | 22.4           | -15.7          | 0.8            | -11.8          |
| -NO <sub>2</sub>                  | 20.0           | -4.8           | 0.9            | 5.8            |
| -SH                               | 2.2            | 0.7            | 0.4            | -3.1           |
| -SO <sub>3</sub> H                | 15.0           | -2.2           | 1.3            | 3.8            |

**Benzenoid Aromatics**

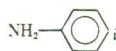
The  $\delta$  value of a carbon atom <sup>i</sup>C can be calculated as the sum of a series of constants such that

$$\delta = 128.5 + A$$

where A is the sum of the increments allowed for the substituents at positions 1, 2, 3, and 4 (Table 6) and 128.5 is the  $\delta$  value for benzene. Two examples are



$$\begin{aligned} \delta^i &= 128.5 + A_1 + 2 \times A_3 \\ &= 128.5 + 2.1 + 2 \times 0.9 \\ &= 132.4 \text{ (observed 132.2)} \end{aligned}$$



$$\begin{aligned} \delta^i &= 128.5 + A_4 \\ &= 128.5 - 9.5 \\ &= 119.0 \text{ (observed 119.0)} \end{aligned}$$

**Aldehydes and Ketones (saturated and  $\alpha,\beta$ -unsaturated)**

The  $\delta$  value of the carbonyl carbon atom can be calculated as the sum of a series of constants such that

**Table 7. Increments for A for the General Structure**

$$-C_{\gamma}-C_{\beta}-C_{\alpha}-C(=O)-C_{\alpha'}-C_{\beta'}-C_{\gamma'}$$

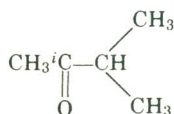
| Substituent                    | Increments                       |                                 |                                    |
|--------------------------------|----------------------------------|---------------------------------|------------------------------------|
|                                | A <sub><math>\alpha</math></sub> | A <sub><math>\beta</math></sub> | A <sub><math>\gamma</math></sub> * |
| -C.sp <sup>3</sup>             | 6.5                              | 2.6                             | 1.0                                |
| -C <sub>6</sub> H <sub>5</sub> | -1.2                             | 0.0                             | ...                                |
| -CH=CH <sub>2</sub>            | -0.8                             | 0.0                             | ...                                |
| -2-furanyl                     | -12.0                            | ...                             | ...                                |

\* When C <sub>$\alpha$</sub> C <sub>$\beta$</sub>  = CH=CH-

$$\delta^i = 193.0 + A$$

where A is the sum of the increments for substituents in the  $\alpha$ ,  $\beta$ , and  $\gamma$  positions (Table 7) and 193.0 is an assumed  $\delta$  value for methanal. Two examples are

$$\begin{aligned} \text{CH}_3\text{CH}=\text{CH}^i\text{CHO} \quad \delta^i &= 193.0 + A \\ &= 193.0 + \alpha + \gamma \\ &= 193.2 \text{ (observed 192.4)} \end{aligned}$$



$$\begin{aligned} \delta^i &= 193.0 + 2\alpha + 2\beta \\ &= 193.0 + 13.0 + 5.2 \\ &= 211.2 \text{ (observed 212.1)} \end{aligned}$$

**Carboxylic Acids and Esters**

The  $\delta$  value of the carbonyl carbon can be calculated in the usual way from the equation

$$\delta^i = 166 + A$$

where 166 is the assumed  $\delta$  value for methanoic acid. Values for A are given in Table 8, and two sample calculations are given below

$$\begin{aligned} \text{CH}_3\text{COCH}_2\text{CH}_2^i\text{COCH}_2\text{CH}_2\text{CH}_3 \quad \delta^i &= 166 + \alpha + \beta + X \\ &= 166 + 11 + 3 - 5 \\ &= 175 \text{ (observed 172.7)} \end{aligned}$$

$$\begin{aligned} \text{CH}_2=\text{CH}^i\text{COOMe} \quad \delta^i &= 166 + \alpha + X \\ &= 166 + 5 - 5 \\ &= 166 \text{ (observed 165.5)} \end{aligned}$$

**Table 8. Increments for A for the General Structure**

$$-C_{\gamma}-C_{\beta}-C_{\alpha}-C(=O)-O-X$$

| Substituents                   | Increments |         |          |    |
|--------------------------------|------------|---------|----------|----|
|                                | $\alpha$   | $\beta$ | $\gamma$ | X  |
| -C.sp <sup>3</sup>             | 11         | 3       | -1       | -5 |
| -C <sub>6</sub> H <sub>5</sub> | 6          | 1       | ...      | -8 |
| -CH=CH <sub>2</sub>            | 5          | ...     | ...      | -9 |

**Amides**

The  $\delta$  value for the amide carbon atom can be calculated in the usual way from the equation

$$\delta^i = 165 + A$$

where 165 is an assumed  $\delta$  value for the methanamide. A increments are given in Table 9; note that the syn-carbon atoms (designated  $\alpha''$ ) are shielded by 3-5 ppm with respect to the anti-carbon atoms ( $\alpha'$ ). An example is

$$\begin{aligned} \text{C}_6\text{H}_5\text{NH}^i\text{COCH}_2\text{CH}_2\text{CH}_3 \quad \delta^i &= 165 + \alpha + \beta + \alpha' \\ &= 165 + 7.7 + 4.5 - 4.5 \\ &= 172.7 \text{ (observed 172.1)} \end{aligned}$$

