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.

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

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

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

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

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

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

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

Acknowledgment

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A Short Set of ¹³C-NMR Correlation Tables

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Many student textbooks in discussion of ¹³C-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 ¹³C nuclei giving the familiar wide spread of resonance of over 200 ppm. This is usually followed by a short discussion of the relationship between δ values and (1) mode of hybridization, (2) inductive effects, (3) mesomeric effect and then by provision of tables giving broad ranges of values for ¹³C 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 ¹³C spectroscopy than ¹H-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 ¹³C-NMR spectroscopy. However, the space devoted to the calculation of δ 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 δ values for ¹³C 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 "13C-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 δ values are taken where possible from spectra determined in CDCl3 using TMS as internal standard.

Alkanes and Substituted Alkanes

The δ value of a carbon atom ${}^{i}C$ 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 α , β , or γ to the ¹³C atom in question, B is the sum of the branching corrections and -2.3 is the δ 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.
- 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)

	Increments						Increments		
Substituent	α	β	γ	Substituent	α	β	γ		
—C.sp ³	9.1	9.4	-2.5	-N<	28.3	11.3	-5.1		
c <u>=</u> c	4.4	5.6	-3.4	-N=	30.7	5.4	-7.2		
c=c	19.5	6.9	-2.1	-NO ₂	61.6	3.1	-4.6		
—C ₆ H ₅	22.1	9.3	-2.6	—S—	10.6	11.4	-3.6		
—CI	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		
	-7.2	10.9	-1.5	COO-	24.5	3.5	-2.5		
0	21.4	2.8	-2.5	-coo-	22.6	2.0	-2.8		
-0-	49.0	10.1	-6.2	-con<	22.0	2.6	-3.2		
OCO	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 γ -substituents in calculating the value of A for

The above points are illustrated by the following calculations.

(1)
$$CH_3CH_2^iCH(OH)CH_3$$

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

$$= -2.3 + (2\alpha^1 + \alpha^2 + \beta + \gamma) + B$$

$$= -2.3 + (9.1 \times 2 + 49.0 + 9.4 + 0.0) + (-3.7)$$

$$= 70.6 \text{ (observed 68.8)}$$
(2) $CH_3^iCH_2CH(OH)CH_3$
$$\delta^i = -2.3 + (9.1 \times 2 + 9.4 + 10.1 + 0.0) + (-2.5)$$

$$= 32.9 \text{ (observed 32.3)}$$

(3)
$$(CH_2OH)_3^i CNO_2$$
 $\delta^i = 2.3 + (9.1 \times 3 + 61.6 + 30.3 + 0.0) + (-8.4 \times 3 - 1.5) = 90.2 \text{ (observed 94.9)}$
(4) $(CH_3)_3^i CCOCH_3$ $\delta^i = -2.3 + (9.1 \times 3 + 22.5)$

+9.4 + 0.0) + (-15.0)

= 41.9 (observed 44.3)

 $+ 18.8) + (-3.7 \times 2)$

= 76.7 (observed 77.0)

Alkenes and Alkene Derivatives

OCH₃

The δ value of a carbon atom ${}^{i}C$ 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 α , β , and γ to ${}^{\rm i}{\rm C}$, B is the correction term for the type of disubstitution and 122.8 is the observed δ 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

(E)—CH₃CH=
i
CHCH₂CH₃ δ^{i} = 122.8 + A + B
= 122.8 + (α + β + α')
= 122.8 + (10.6 + 7.2 - 7.9)
= 132.7 (observed 132.7)

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

	The number of substituents (other than H) on the α -substituents.					
¹³ C atom						
observed	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 ₂ H,CO ₂ R,NO ₂					
secondary	-C ₆ H ₅ , -CHO, -CONH ₂ , -CH ₂ X*					
tertiary	—COR					

^{*} X = OH, -NH₂, -SH or halogen.

Table 3. Increments for A and B for the General Alkene Structure (5) — C_{β} — C_{α} — $^{\prime}$ C—C— $C_{\alpha^{1}}$ — $C_{\beta^{1}}$

Position of substitution	Increments A	Type of disubstitution	Increments B	
α	10.6	α, α' cis	-1.1	
β	7.2	α, α gem	-4.8	
γ	-1.5	α', α' gem •	+2.5	
α'	-7.9	β , β gem	- 2.3	
β'	-1.8			
γ'	+1.5			

Table 4. Increments for A for the General Alkene Derivative Structure (1, 6) $X \longrightarrow CH(\alpha) \longrightarrow CH_2(\beta)$

Substituent	Incre	ements		Increments	
X	α	β	Substituent	α	β
—CI	3.3	-5.6	-CH ₂ Y*	12	-5
-NCOR ₂	7.2	-28.5	-CH ₂ CO ₂ H	6.9	-4.6
-NO ₂	22.8	-0.4	—CH ₂ CN	5.9	-2.1
—Ņ≡	18.9	-26.2	C ₆ H ₅	13.0	-10.5
—OCH₃	31.0	-38.2	—C≡N	-15.6	15.1
-OCOCH ₃	18.9	-26:4	—CO₂R	6.0	8.0
-CH ₃	13.4	-6.9	—COCH₃	14.9	6.7
— <i>t-</i> Bu	26.9	-13.0	-CHO	15.8	14.8
			-CON	9.6	3.

^{*} Y = an electronegative atom or group

For Table 4, two examples are

Note that ${}^{i}C$ in the part-structure (Z)—R—CH=CH— ${}^{i}C \le$ is shielded by between 4 and 9 ppm.

Alkynes

The δ value of a carbon atom iC can be calculated as the sum of a series of constants such that

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

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

BuⁿⁱC=CCOCH₃
$$\delta^{i} = 71.9 + (\alpha + \beta + \alpha')$$
$$= 71.9 + (6.9 + 4.8 + 4.0)$$
$$= 87.6 \text{ (observed } 87.0)$$
$$p\text{-ClC}_{6}\text{H}_{4}\text{--}{}^{i}\text{C}=\text{C-CH}_{3}$$

$$\delta^{i} = 71.9 + (12.7 - 5.7)$$
$$= 78.9 \text{ (observed } 79.6)$$

Table 5. Increments for A for the General Structure (8) $-C_{\beta}-C_{\alpha}-{}^{\prime}C=C-C_{\alpha}-C-B^{-1}$

		u	Р		
	Increments				
Substituents	α	α'	β	β'	
—C.sp ³	6.9	-5.7	4.8	2.3	
-CH ₂ OH	11.1	1.9			
—COCH₃	31.4	4.0			
C ₆ H ₅	12.7	6.4			
-CH-CH ₂	10.0	11.0			

Table 6. Increments for A for the General Structure

Substituent	Increments					
X	A ₁	A_2	A ₃	A_4		
CH ₃	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 ₂	7.6	-1.8	-1.8	-3.5		
—C≡CH	-6.1	3.8	0.4	-0.2		
C ₆ H ₅	13.0	-1.1	0.5	-1.0		
-CHO	8.6	1.3	0.6	5.5		
-COCH ₃	9.1	0.1	0.0	4.2		
—CO₂H	2.1	1.5	0.0	5.1		
CO ₂ -	7.6	0.8	0.0	2.8		
—CO₂R	2.1	1.2	0.0	4.4		
—CONH₂	5.4	-0.3	-0.9	5.0		
-CN	-15.4	3.6	0.6	3.9		
—CI	6.2	0.4	1.3	-1.9		
—OH	26.9	-12.7	1.4	-7.3		
—OCH₃	31.4	-14.4	1.0	-7.7		
OC_6H_5	29.1	-9.5	0.3	5.3		
-OCOCH ₃	23.0	-6.4	1.3	-2.3		
$-NH_2$	18.7	-12.4	1.3	-9.5		
$-N(CH_3)_2$	22.4	-15.7	0.8	-11.8		
-NO ₂	20.0	-4.8	0.9	5.8		
—SH	2.2	0.7	0.4	-3.1		
—SO₃H	15.0	-2.2	1.3	3.8		

Benzenoid Aromatics

The δ value of a carbon atom $\,^i\mathrm{C}$ 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 δ value for benzene. Two examples are

$$\delta^{i} = 128.5 + A_{1} + 2 \times A_{3}$$

$$= 128.5 + 2.1 + 2 \times 0.9$$

$$= 132.4 \text{ (observed } 132.2)$$

NH₂
$$\delta^i = 128.5 + A_4$$

= 128.5 - 9.5
= 119.0 (observed 119.0)

Aldehydes and Ketones (saturated and α, β -unsaturated)

The δ 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

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

where A is the sum of the increments for substituents in the α , β , and γ positions (Table 7) and 193.0 is an assumed δ value for methanal. Two examples are

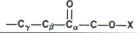
Carboxylic Acids and Esters

The δ value of the carbonyl carbon can be calculated in the usual way from the equation

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

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

Table 8. Increments for A for the General Structure



	Increments					
Substituents	α	β	γ	X		
$-C.sp^3$	11	3	-1	-5		
-C ₆ H ₅	6	1		-8		
-CH=CH ₂	5			-9		

Amides

The δ 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 δ value for the methanamide. A increments are given in Table 9; note that the syn-carbon atoms (designated α'') are shielded by 3–5 ppm with respect to the anti-carbon atoms (α'). An example is

$$C_6H_5NH^iCOCH_2CH_2CH_3$$
 $\delta^i = 165 + \alpha + \beta + \alpha'$
= 165 + 7.7 + 4.5 - 4.5
= 172.7 (observed 172.1)

[•] When $C_{\alpha}C_{\beta} = CH = CH$

Table 9. Increments for the General Structure

Substituents	α	β	γ	α'	β'
—C.sp ³	7.7	4.5	-0.7	-1.5	-0.3
-C ₆ H ₅	4.7			-4.5	
-vinyl	3.3		***		

Nitriles

The δ^i value for the R—C \equiv N nitrile-carbon atom is fairly constant. The examples listed in Table 10 indicate the way in which the δ value varies in different environments.

More Complex Examples

A severe limitation of the additivity rules described here is that they cover only benzenoid aromatics. However, additivity rules have been published for many other polycyclic benzenoid and heterocyclic systems² including pyridine (12), pyrrole (13, 14), furan (15, 16), and thiophene (15, 17). The use of the tables has been illustrated so far by reference to very simple compounds. Fair predictions (± 4 ppm) of δ values can be made for carbons in the more complicated structures likely to be encountered in undergraduate projects and postgraduate research work.

For I.

$$\begin{split} \delta &= -2.3 + A + B \\ &= -2.3 + (\alpha^1 + \alpha^2 + \alpha^3 + 2\beta^1 + \beta^2 + 2\gamma^1) \\ &+ (3^\circ \to 3^\circ + 3^\circ \to 2^\circ + 3 \to 2^\circ) \end{split}$$

Table 10. Examples of the Variation of δ Values for Nitriles in Different Environments

			,		8
Substituent	value	Substituent	o value	Substituent	value
—Me	117.7	—CH₂CI	115.7	p-C ₆ H ₄ NO ₂	112.2
Et	120.8	—vinyl	117.2	-2-furanyl	111.7
— <i>i</i> -Pr	123.7	C ₆ H ₅	118.7	—cinnamyl	118.3

$$= -2.3 + (9.1 + 22.0 + 28.3 + 9.4 \times 2 + 2.0 + -2.5 \times 2) + (-9.5 - 3.7 - 3.7)$$

$$= 56.0 \text{ (observed 59.8)}$$
(1)

For II

$$\begin{split} \delta &= -2.3 + (2\alpha^1 + 2\alpha^2 + 2\beta^1 + \beta^2 + \beta^3 + 5\gamma^1 + \gamma^2) \\ &+ (4^\circ \to 3^\circ + 4^\circ \to 2^\circ + 4^\circ \to 2^\circ + 4^\circ \to 1^\circ) \\ &= -2.3(18.2 + 98.0 + 18.4 + 10.1 + 11.3 - 12.5 - 6.2) \\ &+ (-15.0 - 8.4 - 8.4 - 1.5) = 101.7 \text{ (observed 97.6)} \end{split}$$

The two examples shown above were taken at random. The close agreement between the calculated and observed values came as a shock to the author who will press his luck no further.

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