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ESTIMATION OF THE CHEMICAL SHIFTS OF OLEFINIC PROTONS USING ADDITIVE INCREMENTS—II

THE COMPILATION OF ADDITIVE INCREMENTS FOR 43 FUNCTIONAL GROUPS

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Abstract—Additive shielding parameters for olefinic protons were derived for 36 functional groups by means of a least squares procedure applied to 4298 chemical shifts. Additional shielding parameters for a further 7 functional groups were obtained by assuming simple additivity. A number of conspicuous exceptions to the calculated values are listed.

INTRODUCTION

IN THE first part of this series, some of us[1] derived 30 additive increments for the calculation of the chemical shifts of olefinic protons by a least squares treatment of 1070 chemical shift values derived from the literature. Although strict additivity of substituent effects in ethylene derivatives is *not* to be expected on general grounds,[2] and the deviations from it have recently been explored by Niwa,[3] we have found the additive increments[1] so useful in practice that we have undertaken a wider literature survey to increase both the reliability (an over fourfold increase in the number of data) and the scope (six additional groups) of the original treatment.

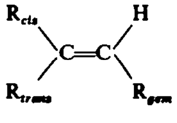
The approximate additivity of substituent effects on the chemical shifts of olefinic protons has been noted and utilised by Goldstein *et al.*[4] and by Tobey,[5] and related studies have been carried out earlier by Jackman and Wiley.[6] However, the present work is based on a number of chemical shift parameters which is approximately *two orders of magnitude* larger than the collections used by the above authors.

RESULTS

Assuming the additivity of substituent effects on the chemical shifts‡ of olefinic protons, one can write the following expression for the chemical shift (δ) of any olefinic proton:

$$\delta = \text{base value} + \sum_i Z_i \qquad \text{(i)}$$

where Z_i are the respective shielding increments for substituents (R) in the *gem*, *cis* and *trans* relationship to the proton.



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‡ All chemical shifts (δ) are in ppm downfield from internal TMS. Negative values for substituent increments denote an upfield shift.

In previous calculations[1] we have taken one of the published values[7] for the chemical shift of ethylene (5·28 ppm) as the base value, which makes the shielding increments for hydrogen zero. In the present instance, the shielding increments for hydrogen were also taken as zero, but for the sake of consistency the base value was taken as the *calculated* value for ethylene (5·25 ppm, see Table 1).*

The data were put into the form of equations

$$F_i(Z_{gem}[I] + Z_{cis}[I] + Z_{trans}[I]) - Y_i = \mathrm{R}_i \qquad \text{(ii)}$$

where I is the number of the substituent, i the number of the system, and Y_i the experimental value. The system of equations was optimized to give a minimum sum of squares of R_i.†

The very large number of data available‡ have allowed us to restrict ourselves to results obtained in carbon tetrachloride and deuterochloroform solutions, although a few data for cyclohexane, tetramethylsilane, benzene and deuteroacetone solutions were also utilised. Further, it was found possible to subdivide certain groups previously treated as single substituents (e.g. "aromatic") into subgroups (see remarks in Table 1). Heteroaromatic systems and 3- and 4-membered rings were not considered.

The above procedure yielded the substituent shielding increments, Z_i, listed in Table 1. These parameters and Eq. (i), with 5·25 ppm as the base value, reproduced the 4298 chemical shifts to the accuracy shown in Table 2. It can be seen that in the vast majority of instances the experimental values are in reasonable agreement with the calculated ones (standard deviation 0·17 ppm). With the notable exception of Z_{gem} for conjugated amino groups (case 30), the Z_i values listed here are comparable with those derived previously for the same substituents,[1] although the number of chemical shift data was increased more than 4-fold. It is therefore likely that any further increase in the number of data used in this fashion would lead only to minor differences in the Z_i factors. It can also be seen from a comparison of Table 2 with Table 4 in part I,[1] that the confidence limits have remained essentially unaltered.

When one considers that the total range of chemical shifts of olefinic protons taken in this work covers 5·72 ppm (see Table 3 for extreme values), the high probability (94%) of calculating the chemical shift of any olefinic proton to ±0·3 ppm can be seen as of obvious practical value. It is worth noting that the error involved due to the assumption of the additive model described ($s = 0·136$ ppm) is no larger than that associated with the *experimental* determination of the chemical shifts i.e. with factors such as concentration and solvent effects and the accuracy of analysis.

Table 4 lists some of the conspicuous exceptions from the calculated values; other examples are given in part I of this series,[1] and in reference 2, chapter 3–3. It is clear that some of the discrepancies (e.g. the second entry in Table 3 and the first entry in

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* We have redetermined the chemical shift of ethylene in CCl_4 using a Varian model HA-100 spectrometer with a frequency counter. The value for a saturated solution at 28° was unchanged on 2-fold, 4-fold and 8-fold dilution and is 5·352 ± 0·001 ppm, which can thus be taken as the chemical shift of ethylene in CCl_4 at infinite dilution. This is in excellent agreement with the value reported by Bothner-By and Naar-Colin[8] (5·350 ppm for a 0·1 molar soln) but is significantly different from other literature values.[1]

† The computation was carried out using a CDC 1604-A computer at the Computation Center of the Eidg. Technische Hochschule, Zurich. The procedure amounts to the solution of 4298 simultaneous equations in 104 unknowns.

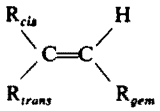
‡ The chemical shift values were drawn from approximately 800 literature references as well as from data obtained in the authors' laboratories.

TABLE 1. ADDITIVE SHIELDING INCREMENTS FOR OLEFINIC PROTONS DERIVED BY THE LEAST SQUARES TREATMENT

The increments "R conjugated" are to be used instead of "R isolated" when either the substituent or the double bond is conjugated with further substituents. The increments "Alkyl-Ring" are to be used when the substituent together with the double bond are a part of a cyclic structure.* The increments "Aromatic fixed" are to be used when the double bond is conjugated with the aromatic ring and is also a part of a ring closed to the aromatic ring (e.g. 1,2-dihydronaphtalene).

The chemical shifts of an olefinic proton ($\delta_{\mathrm{C=C}\diagdown\mathrm{H}}$) in ppm from internal tetramethylsilane are given by:

$$\delta_{\mathrm{C=C}\diagdown\mathrm{H}} = 5{\cdot}25 + Z_{gem} + Z_{cis} + Z_{trans}$$



Substituent R	Z_i for R (ppm)		
	Z_{gem}	Z_{cis}	Z_{trans}
1. —H	0	0	0
2. —Alkyl	0·45	-0·22	-0·28
3. —Alkyl-Ring	0·69	-0·25	-0·28
4. —CH_2O	0·64	-0·01	-0·02
5. —CH_2S	0·71	-0·13	-0·22
6. —CH_2X, X:F, Cl, Br	0·70	0·11	-0·04
7. —CH_2N	0·58	-0·10	-0·08
8. —C=C isolated	1·00	-0·09	-0·23
9. —C=C conjugated	1·24	0·02	-0·05
10. —C≡N	0·27	0·75	0·55
11. —C≡C	0·47	0·38	0·12
12. —C=O isolated	1·10	1·12	0·87
13. —C=O conjugated	1·06	0·91	0·74
14. —COOH isolated	0·97	1·41	0·71
15. —COOH conjugated	0·80	0·98	0·32
16. —COOR isolated	0·80	1·18	0·55
17. —COOR conjugated	0·78	1·01	0·46
18. $-\overset{H}{C}=O$	1·02	0·95	1·17
19. $-\overset{N}{C}=O$	1·37	0·98	0·46
20. $-\overset{Cl}{C}=O$	1·11	1·46	1·01
21. —OR, R : aliphatic	1·22	-1·07	-1·21
22. —OR, R : conjugated	1·21	-0·60	-1·00
23. —OCOR	2·11	-0·35	-0·64
24. —CH_2—C=O; —CH_2—C≡N	0·69	-0·08	-0·06
25. —CH_2-Aromatic-Ring	1·05	-0·29	-0·32
26. —Cl	1·08	0·18	0·13
27. —Br	1·07	0·45	0·55

Table 1—*continued*

Substituent R	Z_i for R (ppm)		
	Z_{gem}	Z_{cis}	Z_{trans}
†28. —I	1·14	0·81	0·88
29. —N—R, R : aliphatic	0·80	−1·26	−1·21
30. —N—R, R : conjugated	1·17	−0·53	−0·99
31. —N—C═O	2·08	−0·57	−0·72
32. —Aromatic	1·38	0·36	−0·07
33. —Aromatic fixed	1·60	—	−0·05
34. —Aromatic *o*-subst.	1·65	0·19	0·09
35. —SR	1·11	−0·29	−0·13
36. —SO_2	1·55	1·16	0·93

* Data for compounds containing 3- and 4-membered rings have not been considered.

† The values in this row are based on data from only 4 substances.

Table 2. The distribution of the discrepancies (Δδ)* between the experimental and calculated values of the chemical shifts of olefinic protons for the 4298 cases investigated

Δδ (ppm) within	% of the 4298 cases
0·17	75·7
0·20	81·3
0·30	94·0
0·50	99·7

* Δδ is approximately represented by a normal distribution. At a standard deviation of 0·169, 75·7% of all systems are within the σ-limit as compared to the theoretical value of 68·3%.

Table 3. Extreme values of chemical shifts encountered among the 4298 cases investigated

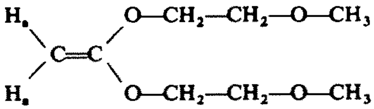
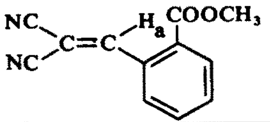
Structure	Solvent	δ_{H_a} (ppm)		Reference
		Exper.	Calculated	
	CCl_4	3·00	2·97	9
	$CHCl_3$	8·72	8·20	10

TABLE 4. SOME SYSTEMS WITH DISCREPANCIES BETWEEN THE EXPERIMENTAL AND CALCULATED VALUES ($\Delta\delta$) EXCEEDING 0·50 PPM

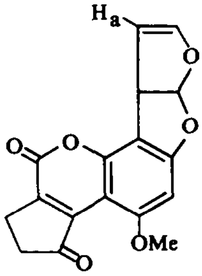
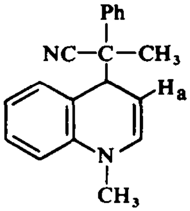
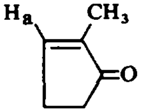
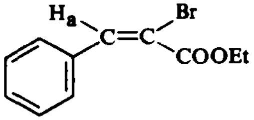
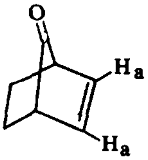
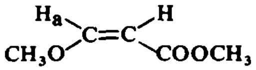
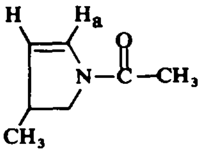
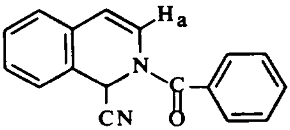
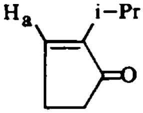
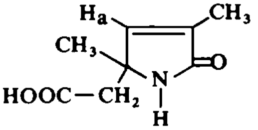
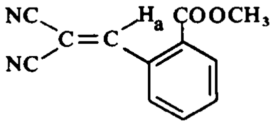
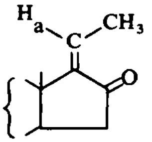
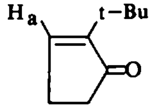
Structure	Solvent	δH_a (ppm)		Reference
		Exper.	Calc.	
	$CDCl_3$	5·48	4·73	11
	$CDCl_3$	4·67	5·31	12
	CCl_4	7·23	6·59	13
	—	8·17	7·54	14
	CCl_4	6·50	5·88	15
	CCl_4	6·40	7·02	16
	$CDCl_3$	6·47	7·09	17

TABLE 4—*continued*

Structure	Solvent	δH_a (ppm)		Reference
		Exper.	Calc.	
	$CDCl_3$	6·69	7·28	12
	CCl_4	7·16	6·59	13
	$CDCl_3$	6·71	6·18	18
	$CHCl_3$	8·72	8·20	10
	$CDCl_3$	5·65 5·70	6·35	19
	CCl_4	7·10	6·59	13

"*Note added in proof.* A further search of the literature revealed a number of larger (up to 1·25 ppm) deviations. The origin of these discrepancies is discussed in Part III of this series (U. E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon and S. Sternhell, *Tetrahedron, in press*)."

Table 4) are due to spatial proximity of magnetically anisotropic groups. However other discrepancies (e.g. the low chemical shifts of the β-protons in cyclopentenone derivatives in Table 4) probably have other origins. We defer the discussion of unusual chemical shifts of olefinic protons to a separate communication.

After the completion of the collection of data for the compilation of the Z_i values listed in Table 1, we have undertaken a separate literature search for less common substituent groups attached to the ethylene residue. Using the Z_i values from Table 1 allowed us to derive the average Z_i values for these additional substituents listed in

Table 5 by simple substitution. Because these data are based on very limited ranges of compounds, the literature sources are also given in Table 5 to enable the reader to judge if these values may be applied to any particular situation.

TABLE 5. SHIELDING INCREMENTS FOR ADDITIONAL FUNCTIONAL GROUPS

Substituent R	Z_i for R (ppm)			Reference
	Z_{gem}	Z_{cis}	Z_{trans}	
$—SF_5$	1·68	0·61	0·49	20
—SCN	0·80	1·17	1·11	21
$—CHF_2$	0·66	0·32	0·21	22
$—CF_3$	0·66	0·61	0·32	22
 $—S—\underset{\overset{\Vert}{O}}{C}—CH_3$	1·41	0·06	0·02	23
—F	1·54	−0·40	−1·02	24
$—PO(OEt)_2$	0·66	0·88	0·67	25

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