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

EXAMPLES OF UTILITY IN NMR STUDIES AND THE IDENTIFICATION OF SOME STRUCTURAL FEATURES RESPONSIBLE FOR DEVIATIONS FROM ADDITIVITY

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Abstract—Examples of utilization of the additive shielding parameters for olefinic protons in making NMR assignments are given and modifications of some published data are suggested. The role of ground-state mesomeric effects on chemical shifts in numerous classes of alkenes is stressed. Some structural features associated with significant deviations from results calculated on the basis of the additivity principle are: (i) unusual juxtaposition of remote functional groups, (ii) planar conjugated carbonyl derivatives, (iii) bicyclic olefins and dienes, (iv) vinyl ethers in which the lone pairs on the oxygen are constrained into certain conformations, (v) vinyl iodides.

INTRODUCTION

IN PREVIOUS communications[1,2] we have derived additive shielding parameters for olefinic protons which reproduce the vast majority[2] of experimentally obtained chemical shifts with a surprisingly high accuracy. In this work we wish to extend the usefulness of this method by pointing out applications in the field of NMR spectroscopy and by identifying, and partially rationalizing, the origin of certain conspicuous deviations from the additivity principle. In the following discussion, all additive shielding increments (Table 1) are from Table 1 of ref. 2.

ADDITIVE SHIELDING INCREMENTS AND NMR ASSIGNMENTS

The usefulness of the additive shielding increments for olefinic protons in structural studies is obvious, particularly in cases where a distinction between isomers is being made. Perhaps somewhat less obvious is their utility in making NMR assignments in cases where the structures themselves are not in doubt.

Hutton and Schaefer[3] assigned the chemical shifts of H_A and H_B in I‡ on the basis of comparison with a selected group of model substances. It can be seen, however, that the same assignments follow from the use of the additive shielding parameters. The important part of the argument is not the (here excellent) agreement between the calculated and experimental values, which would be worsened by the alternative assignment, but the *relative* chemical shifts of the two protons.

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‡ All numbers of compounds are defined in Tables 1 and 2.

Kasiwagi and Niwa[4] have assigned the chemical shifts of the α and β protons in the styrene derivatives II and III. but the calculations based on the additive shielding parameters show that the assignments must be reversed, even though the agreement for the β-proton in the *cis* isomer (II) is not very satisfactory.

The chemical shifts of the exocyclic methylene protons in ketene dimer (IV) have been assigned[5] on the basis of the expectation of the *cisoid* allylic coupling constant being larger than the *transoid* allylic coupling constant. However, we have shown[6] that the reverse relative values of allylic coupling constants would actually be expected in this particular steric situation. This suggested to us[6] that the relative assignments of H_A and H_B should be reversed and it can be seen that our assignments[6] (shown here) are in better agreement with the values calculated with the aid of the additive shielding parameters that the original assignments[5] (marked R for "reversed").

STRUCTURAL FEATURES ASSOCIATED WITH DEVIATIONS FROM ADDITIVITY

In preceding communications[1,2] and elsewhere[7] we have listed a number of compounds where the chemical shifts of olefinic protons show significant deviations from the values calculated by means of the additive shielding parameters. We now wish to discuss a number of structural features which appear to be associated with these apparent anomalies. This should extend the usefulness of the additivity principle for the calculation of chemical shifts of olefinic protons by indicating its limitations. Further, the discrepancies associated with well-defined structural features may serve to define areas of interest in connection with the theory of chemical shifts. In fact, many of the examples quoted below are not derived from the original[1,2] broad survey but from supplementary literature searches for specific structures after certain discrepancies were observed. The additional data refer to carbon tetrachloride, deuterochloroform or hexane solutions.

Before proceeding to discuss the deviations from additivity in terms of structural features we would like to point out that the chemical shifts of the *cis* and *trans* β-protons in numerous classes of alkenes (cases 10, 12–23, 29, 30, 35 and 36 in Table 1 of Ref. 2 and cases 2, 6 and 7 in Table 5 of ref. 2) are best rationalized in terms of ground state mesomerism.[8] This has been pointed out for *some* of these groups of compounds (cf e.g. some references quoted in Section (iv) below) but appears to be ignored in most discussions of chemical shifts.

(i) *Spatial juxtaposition of skeletally remote functional groups.* The chemical shifts of protons marked H_A in V[9] and VI[10] show very large deviations from additivity clearly due to the well documented[11] long-range deshielding effect of the carbomethoxy group in V and the shielding effect of the cyclopropane ring in VI respectively. The latter effect can also be seen to operate in VII[12,13] in a significantly additive manner. i.e. 0·26 + 0·54 = 0·80 ppm. while in VI the deviation is 0·84 ppm.

The above examples are cases where the shielding increment[1,2] is in effect "incompletely described" *and* also the substituent is positioned in a well-defined manner with respect to the olefinic proton. A similar situation is encountered in cases where the substituent is "well described" by its shielding increment, but its position with respect to the olefinic proton is unusual. A good example of this is found in a series of 1-aryl-*cyclo*hexanes (VIII–XI) reported by Garbisch.[14] It can be seen that the additive increments[2] reproduce the chemical shifts of the olefinic protons in phenylcyclohexene

(VIII) and 1-phenyl-4-t.-butylcyclohexene (IX). However, the "buttressing"[15] of the aryl group, either by vicinal substitution as in X, or by the introduction of *ortho* substituents in the phenyl ring, as in XI, causes a large upfield shift for the olefinic proton, obviously due to the shielding region of the benzene ring. In comparing VIII with XI, we have already taken some account of the expected average conformation of the aromatic ring by using the "aromatic *ortho* substituted *cis*" increment instead of the "aromatic *cis*" increment, but the difference (0·36–0·19 = 0·17 ppm), while in the right direction, is clearly not sufficient to compensate for the buttressing of *two ortho* substituents.

Additivity of olefinic chemical shifts is expected to break down for exocyclic protons, where the alicyclic ring has a substituent α to the double bond with a pronounced effect on chemical shifts of olefinic protons. This is exemplified[16] in the enones XII and XIII and is obviously related to the fact that the relatively fixed orientation of the carbonyl group with respect to the olefinic protons is significantly different from the statistical average used[2] in compiling the shielding increments. The mere presence of an *exocyclic* group does not lead to deviation from additivity (XIV).

(ii) *Planar conjugated systems.* As stated previously[2] protons directly attached to the rings of heteroaromatic (as well as, of course, of benzenoid and polycyclic aromatic) compounds were explicitly excluded from the compilations of data which resulted in the set of additive shielding increments for olefinic protons.[2] Doubtful cases, i.e. those where aromaticity, as defined by ring-current, is disputable, were also excluded and it is not unexpected that the chemical shifts of olefinic protons in, e.g. coumarin (XV)[18] and γ-pyrone (XVI)[19] are downfield of the calculated values. Interestingly, the chemical shift of the olefinic proton in *p*-benzoquinone (XVII)[20] is *upfield* of the calculated value. It is probably unsafe to infer the presence or absence of ring-currents from additivity of olefinic chemical shifts, and arguments of this type are more firmly based on consideration of carefully chosen model compounds (cf e.g. the recent work on γ-pyrones[21]), but factors other than ring currents can be invoked. For instance, data for some 5- and 6-membered α,β-unsaturated carbonyl compounds (XVIII–XXI)[17] show that a tendency towards downfield shifts, especially in the β-position, appears to be associated with 5-membered, rather than 6-membered, rings.

In XVIII–XXI, there is no possibility for continuous cyclic delocalisation (i.e. aromaticity) and we conclude that the greater planarity of the 5-membered rings is the factor involved. The mechanism of the effect could be the positioning of the olefinic protons closer to the plane of the carbonyl bond, where anisotropic deshielding is at a maximum, but we favour the increased importance of ground-state mesomerism as discrepancies of the order of 0·7 ppm (direct comparison of the β-proton shifts in the series XVIII–XXI) are too great to be accounted for by models on long-range shielding effects alone.[22]

In summary, the important practical result emerges that the additivity principle may be unreliable when applied to conjugated carbonyl derivatives, constrained in planar configurations.

(iii) *Cycloalkenes.* As stated previously (cf footnote to Table 1 in ref. 2) cyclopropene and cyclobutene derivatives were excluded from the set of data used in compiling the additive increments because it was felt that angular strain and the resultant rehybridisation could make these values atypical. The chemical shift of the olefinic protons in cyclopropene (7·01 ppm)[23] is indeed very abnormal, but the olefinic

TABLE 1. CHEMICAL SHIFTS OF OLEFINIC PROTONS

All chemical shifts are in ppm ex TMS. Δ denotes experimental value–calculated value. Additive shielding increments are from table 2 in ref. 2

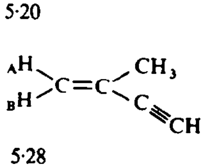
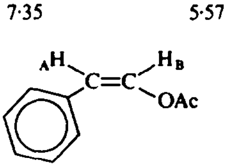
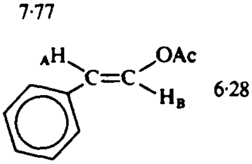
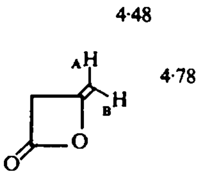
No.	Reference	Structure	Calculated chemical shifts
I	3		H_A: 5·25 −0·22 (alkyl cis) 0·12 (C≡C trans) 5·15 (Δ = 0·05) H_B: 5·25 −0·28 (alkyl trans) 0·38 (C≡C cis) 5·35 (Δ = −0·07)
II	4		H_A: 5·25 1·38 (Aromatic gem) −0·64 (OCOR trans) 5·99 (Δ = 1·36) Reversing assignments: Δ = −0·42 H_B: 5·25 −0·07 (Aromatic trans) 2·11 (OCOR gem) 7·29 (Δ = −1·72) Reversing assignments: Δ = 0·06
III	4		H_A: 5·25 1·38 (Aromatic gem) −0·35 (OCOR cis) 6·28 (Δ = 1·49) Reversing assignments: Δ = 0·00 H_B: 5·25 0·36 (Aromatic cis) 2·11 (OCOR gem) 7·72 (Δ = −1·44) Reversing assignments: Δ = 0·05
IV	5, 6		H_A: 5·25 −0·25 (alkyl-ring cis) −0·64 (OCOR trans) 4·36 (Δ = 0·12) (R = 0·42) H_B: 5·25 −0·28 (alkyl-ring trans) −0·35 (OCOR cis) 4·62 (Δ = 0·16) (R = 0·14) or. alternatively: H_A: 5·25 −0·08 (CH_2CO cis) −0·64 (OCOR trans) 4·53 (Δ = −0·05) (R = 0·25)

TABLE 1—*continued*

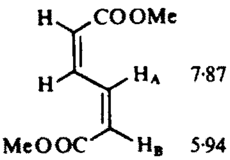
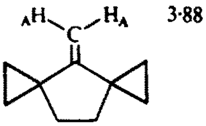
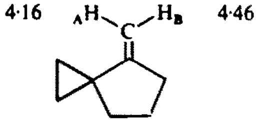
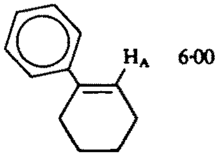
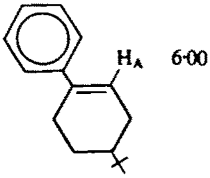
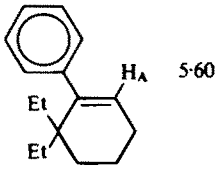
No.	Reference	Structure	Calculated chemical shifts
			H_B: 5·25 −0·06 (CH_2CO trans) −0·35 (OCOR cis) 4·84 (Δ = −0·06) (R = 0·36)
V	9		H_A: 5·25 1·24 (C═C conj. gem) 0·46 (COOR conj. trans) 6·95 (Δ = 0·92) H_B: 5·25 −0·05 (C═C conj. trans) 0·78 (COOR conj. gem) 5·98 (Δ = −0·04)
VI	10		H_A: 5·25 −0·25 (alkyl-ring cis) −0·28 (alkyl-ring trans) 4·72 (Δ = −0·84)
VII	12, 13		H_A and H_B = 4·72 (as for VI) ΔH_A = −0·54 ΔH_B = −0·26
VIII	14		H_A: 5·25 0·69 (alkyl-ring gem) −0·28 (alkyl-ring trans) 0·36 (aromatic cis) 6·02 (Δ = −0·02)
IX	14		H_A: as for VIII
X	14		H_A = 6·02 (as for VIII) (Δ = −0·42)

TABLE 1—*continued*

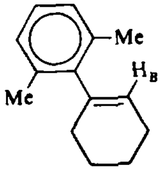
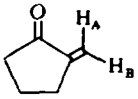
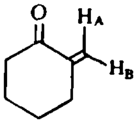
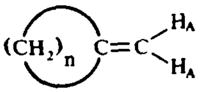
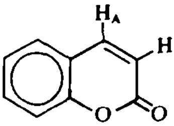
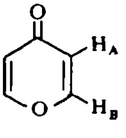
No.	Reference	Structure	Calculated chemical shifts
XI	14	 5·40	H_B: 5·25 0·69 (alkyl-ring gem) −0·28 (alkyl-ring trans) 0·19 (aromatic ortho-substcis) 5·85 (Δ = −0·45)
XII	16	 5·82 5·24	H_A: 5·25 −0·28 (alkyl-ring trans) 1·12 (CO cis) 6·09 (Δ = −0·27) H_B: 5·25 −0·25 (alkyl-ring cis) 0·87 (CO trans) 5·87 (Δ = −0·63)
XIII	16	 5·72 5·04	H_A: 6·09 (as for XII), Δ = −0·37 H_B: 5·87 (as for XII), Δ = −0·83
XIV	17	 n H_A 3 4·70 4 4·82 5 4·55	H_A: 5·25 −0·25 (alkyl-ring cis) −0·28 (alkyl-ring trans) 4·72
XV	18	7·72  6·42	H_A: 5·25 1·60 (aromatic fixed gem) 0·46 (COOR conjugated trans) 7·31 (Δ = 0·41) H_B: 5·25 −0·05 (aromatic fixed trans) 0·78 (COOR conjugated gem) 5·98 (Δ = 0·44)
XVI	19	 6·48 8·05	H_A: 5·25 1·06 (CO conjugated gem) −1·00 (OR. R conj.. trans) 5·31 (Δ = 1·17) H_B: 5·25 0·74 (CO conjugated trans) 1·21 (OR. R conj.. gem) 7·20 (Δ = 0·85)

TABLE 1—*continued*

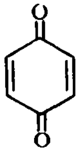
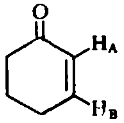
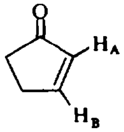
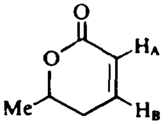
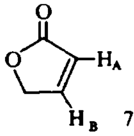
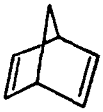
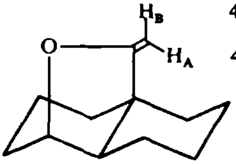
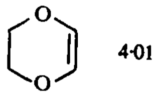
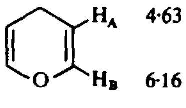
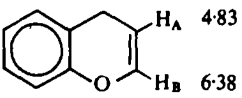
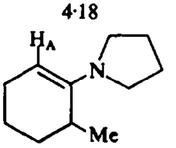
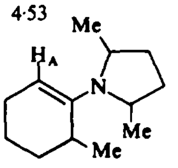
No.	Reference	Structure	Calculated chemical shifts
XVII	20	 6·72	5·25 1·06 (CO conj. gem) 0·74 (CO conj. trans) 7·05 (Δ = −0·33)
XVIII	17	 H_A 5·93 H_B 6·88	H_A: 5·25 1·10 (CO gem) −0·28 (alkyl-ring trans) 6·07 (Δ = −0·14) H_B: 5·25 0·87 (CO trans) 0·69 (alkyl-ring gem) 6·81 (Δ = 0·07)
XIX	17	 H_A 6·10 H_B 7·71	H_A: 6·07 (as for XVIII). Δ = 0·03 H_B: 6·81 (as for XVIII). Δ = 0·90
XX	17	 H_A 5·89 H_B 6·94	H_A: 5·25 0·80 (COOR gem) −0·28 (alkyl-ring trans) 5·77 (Δ = 0·12) H_B: 5·25 0·55 (COOR trans) 0·69 (alkyl-ring gem) 6·49 (Δ = 0·45)
XXI	17	 H_A 6·15 H_B 7·63	H_A: 5·77 (as for XX). Δ = 0·38 H_B: 6·49 (as for XX). Δ = 1·14
XXII	24	 6·65	5·25 0·69 (alkyl-ring gem) −0·28 (alkyl-ring trans) 5·66 (Δ = 0·99)
XXIII	25	 H_B 4·88 H_A 4·35	H_A: 5·25 −0·25 (alkyl-ring cis) −1·21 (OR trans) 3·79 (Δ = 0·56) H_B: 5·25 −0·28 (alkyl-ring trans) −1·07 (OR cis) 3·90 (Δ = 0·98)

Table 2—*continued*

No.	Reference	Structure	Calculated chemical shifts
XXIV	26		5·25 1·22 (OR gem) −1·21 (OR trans) 5·26 (Δ = −1·25)
XXV	27		H_A: 5·25 0·69 (alkyl-ring gem) −1·00 (OR conjugated trans) 4·94 (Δ = −0·31) H_B: 5·25 −0·28 (alkyl-ring trans) 1·21 (OR conjugated gem) 6·18 (Δ = −0·02)
XXVI	28		H_A: 5·25 1·05 (CH_2-Aromatic-ring gem) −1·00 (OR conjugated trans) 5·30 (Δ = −0·47) H_B: 5·25 −0·32 (CH_2-Aromatic-ring trans) 1·21 (OR conjugated gem) 6·14 (Δ = 0·24)
XXVII	29		H_A: 5·25 0·69 (alkyl-ring gem) −0·28 (alkyl-ring trans) −1·26 (NR_2 cis) 4·40 (Δ = −0·22)
XXVIII	29		H_A: 4·40 (as for XXVII). Δ = 0·13

protons in cyclobutene resonate at 5·97 ppm,[23] i.e. not very far from the calculated value of 5·66 ppm.*

The additivity principle clearly breaks down in norbornadiene (XXII)[24] and in several related bicyclic olefins and dienes.[24] It is possible that the particularly large deviation from the calculated values observed in norbornadiene may be related to

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* The chemical shifts of the olefinic protons in cyclopentene, cyclohexene and cycloheptene[23] are within 0·1 ppm of the calculated values.

the overlap of π-electron systems which has already been proposed[24] as a cause of other abnormal chemical shifts in these systems.

(iv) *Vinyl ethers and enamines.* The pronounced downfield shift of the olefinic protons in the vinyl ether derivative of *trans*-decalin (XXIII) relative to simple alkylvinyl ethers has been rationalized[25] in terms of steric inhibition of mesomeric electron donation. It can be seen that this effect is also reflected in a marked deviation from additivity (Table 1). In 1,4-dioxene (XXIV),[26] the olefinic protons resonate markedly *upfield* of the calculated values (Table 1). Inspection of models reveals that in the half-chair conformation, one of the lone pairs on each of the oxygen atoms is almost exactly parallel with the $2p_z$ orbitals of the double bond. We therefore conclude that the upfield shift is due to exceptionally efficient electron donation and that 1,4-dioxene probably exists in the half-chair conformation. Some support for this interpretation can be obtained by considering parallel, although less pronounced, deviations from additivity in γ-pyran (XXV)[27] and 2,3-chromene (XXVI).[28]

In view of the large deviations from additivity observed in the examples above and the apparent sensitivity of the chemical shifts of the β-protons in vinyl ethers to the average conformation of the oxygen lone pairs with respect to the plane of the double bond, it is rather surprising that in the large majority of vinyl ethers the chemical shifts of the olefinic protons can be predicted with accuracy better than 0·3 ppm by the additivity relationships. This suggests that the average conformation of the —OR groups is not very sensitive to the nature of the R group and the other substituents on the ethylene residue. Gurowitz and Joseph[29] have rationalized the differences in the chemical shifts of olefinic protons in the enamines (XXVII and XXVIII) and some related compounds in terms of steric inhibition of electron donation, i.e. in a manner analogous to the arguments used above for vinyl ethers. It can be seen that, for the examples quoted here, the effect is not very pronounced in terms of deviations from the additivity principle (Table 1), but the shifts are in the expected direction. Clearly, unusual conformations should be taken into consideration when applying the additivity principle to the chemical shifts of olefinic protons in vinyl ethers and enamines. It is worth noting that the differences in chemical shifts of the olefinic protons between XXVII and XXVIII are caused by a buttressing effect similar to that observed in XI (cf above).

(v) *Vinyl iodides.* The shielding increments for iodine in Table 1 reference 2 were derived from data for only four substances namely vinyl iodide (XXIX)[30] and three isomeric iodopropenes (XXX-XXXII).[31] In connection with the investigation of oxidation of hydrazones with iodine[32] we have prepared* some further simple vinyl iodides (XXXIII–XXXIX) and tabulated the pertinent NMR data in Table 2. The shielding increments for iodine were then derived by simple subtraction (cf footnote in Table 2). With the exception of compounds XXIX, XXX, XXXI and XXXIX the assignments of chemical shifts are based on the relative magnitudes of long-range coupling constants[31,33] and alternative assignments cannot therefore be excluded. It can be seen that the alternative values of the shielding parameters in iodocompounds with terminal methylene groups, i.e. XXXII–XXXIV are not unreasonable and an argument could be made for reversing the assignments in XXXIV for the sake of consistency (cf *supra*). However, in the isomeric 2-iodobutenes (XXXV and XXXVI)

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* Details of the preparation and properties of these compounds will be given elsewhere.

TABLE 2. SHIELDING INCREMENTS FOR THE OLEFINIC PROTONS IN VINYL IODIDES

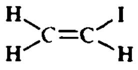
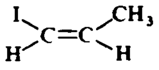
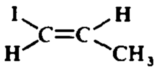
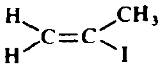
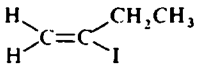
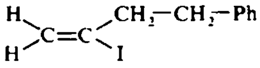
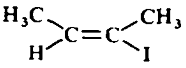
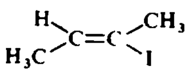
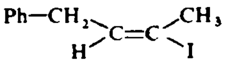
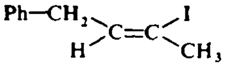
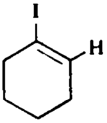
No.	Structure and experimental chemical shifts[a]	Shielding increments for the iodo group (Z)[b]
XXIX	6·19 6·45  6·48	Z_{gem} = 1·23 Z_{cis} = 0·94 Z_{trans} = 1·20
XXX	6·31  6·29	Z_{gem} = 1·34 Z_{trans} = 0·59
XXXI	6·11  6·52	Z_{gem} = 1·08 Z_{cis} = 0·82
XXXII	5·94 *or* 5·59 5·59 *or* 5·94 	Z_{cis} = 0·62 *or* 0·97 Z_{trans} = 0·91 *or* 0·56
XXXIII	5·99 *or* 5·62 5·62 *or* 5·99 	Z_{cis} = 0·65 *or* 1·02 Z_{trans} = 0·96 *or* 0·59
XXXIV	5·61 *or* 5·90 5·90 *or* 5·61 	Z_{cis} = 0·93 *or* 0·64 Z_{trans} = 0·58 *or* 0·87
XXXV	6·15 *or* 5·46 	Z_{cis} = 0·73 *or* 0·04
XXXVI	5·46 *or* 6·15 	Z_{trans} = −0·02 *or* 0·67
XXXVII	6·26 *or* 5·52 	Z_{cis} = 0·84 *or* 0·10
XXXVIII	5·52 *or* 6·26 	Z_{trans} = 0·04 *or* 0·78

TABLE 2—*continued*

No.	Structure and experimental chemical shifts	Shielding increments for the iodo group $(Z)^b$
XXXIX	 6·33	Z_{cis} = 0·67[c]

[a] The experimental chemical shifts for compounds prepared in these laboratories (XXXIII–XXXIX) refer to approximately 5% solutions in carbon tetrachloride and were obtained with a Varian HA-100 spectrometer.

[b] The shielding increments were calculated by using the additive shielding increments from Table 1, reference 2. E.g. the Z_{trans} value for XXX was obtained by subtracting the calculated value for H-2 in propene (5·25 + 0·45 for alkyl-gem = 5·70) from the experimental value for H-2 in 1-iodopropene (6·29). Alternative values of the shielding increments refer to the alternative values of experimental chemical shifts in the second column.

[c] Alternatively, the chemical shift of the olefinic protons in cyclohexene (5·59)[23] can be subtracted from 6·40 to give Z_{cis} = 0·74.

and 2-iodo-4-phenylbutenes (XXXVII and XXXVIII) one of the shielding parameters in each pair *must* be abnormally small. We cannot rationalize this result and point out that other features of the NMR spectra of XXX–XXXII are also difficult to explain.[31] Clearly, caution is necessary in the use of the additive shielding increments in derivatives of vinyl iodide.

(vi) *Conclusions.* The great majority of significant deviations from additivity observed for the 4298 chemical shift data used to compile the additive shielding increments,[2] and for other data found subsequently, fall into one of the five categories of exceptions listed above. On purely statistical grounds one must therefore conclude that the probability of a deviation from additivity greater than 0·30 ppm is smaller than 5% (Ref. 2) if the above exceptional structural features are allowed for. It can also be seen from the above discussion that consideration of deviations from additivity, and some of the regular features associated with the shielding increments, leads to an increasing semiquantitative appreciation of some of the causes of chemical shifts. In particular, we conclude that ground state mesomerism offers the best rationalization of some trends in numerous groups of olefinic compounds.

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