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INDUCTIVE SUBSTITUENT CONSTANTS σ_I^J FROM OLEFINIC GEMINAL ^1H, ^1H NMR COUPLING CONSTANTS

RUDOLF KNORR
Institute of Organic Chemistry, University of Munich, Karlstr. 23, D-8000 München 2, Germany

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Abstract—Theoretical and experimental arguments are presented supporting the postulate that olefinic NMR coupling constants $^2J_{HH}$ are insensitive to β-substituent influences on the olefinic π orbital. A new set of substituent constants, σ_I^J, is proposed to measure directly the inductive substituent effect transmitted by σ-bonds. The previously available range of inductive substituent constants can be appreciably extended in this way. Comparisons of σ_I^J with other observables and parameters for selected substituents are made as a test of consistency.

The quantification of substituent electronic effects by empirical linear free energy relationships is well established.[1] Extensive work by many research groups has shown that a linear combination of polar (σ_I) and resonance (σ_R) substituent parameters constitutes a suitable approach.[2] Resonance interactions, as transmitted through π-orbital systems, may be measured by σ_R^0 substituent constants which have recently gained improvement and reliability from IR intensities.[3] Of numerous efforts to apply new techniques for the re-evaluation of σ_I constants, only one[4] may by singled out which enabled Taft and associates[5] to meet the challenge of gas-phase acidities by calling on polarizability[6] effects.

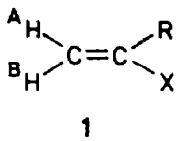
Chemical bonds of σ-symmetry might be thought to transmit the inductive effect (I_σ) of a substituent, thus providing an interpretation of σ_I substituent constants. However, contributions to σ_I from hyperconjugation[7] and field effects[8,9] have been suspected on many occasions. Not even a rough measure of the pure σ-inductive effect I_σ appears to have been generally accepted, although this would be of great value because of its relation to molecular electrical charges and their various consequences.

As a first step to provide such a measure at least approximately, the idea is presented here that the substituent dependence of *olefinic* geminal inter-proton coupling constants $^2J_{HH}$ might serve this purpose.

RESULTS

Theoretical models

Geminal ^{1}H-NMR coupling constants ^2J (H^A, H^B) of protons attached to tetracovalent (sp^3) C atoms are known to depend on the presence and conformation of adjacent π-orbital systems[10,11] (e.g. by hyperconjugation). Geminal protons at trigonal (sp^2) C atoms in a terminal olefin 1, being held in a sterically rigid position, offer a much better model for the separation of π- and σ-orbital effects. Conformational changes like decoupling of π-systems as in 2 are still possible but occur rather remotely and, therefore, mediated mainly by the π-bond.



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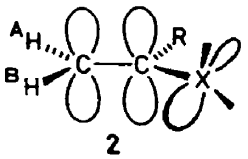

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The theoretical dependence of $^2J(H^A, H^B)$ on σ and π interactions with the substituents X has been analyzed at different levels of sophistication. Pople and Bothner-By[12] in a lucid analysis succeeded in accounting satisfactorily for the experimentally observed trends without recourse to the olefinic π-bond; predominant interaction of increasingly electronegative β-substituents R and X with the antisymmetrical $\pi(CH_2)$ combination of σ-orbitals results in more negative ^2J values. The same conclusions were reached using the β-substituent as a perturbation at trigonal carbon,[13] and omission of π-effects proved successful also in *ab initio* calculations.[14] Similarly, π-contributions to olefinic ^2J were found to be less significant than the σ-bond transmitted part, using localized spin-orbital[15] and semiempirical MO theories,[16] with substituent effects operating almost exclusively on the σ-contribution.[16,17]

Consequently the change from a coplanar conformation like 1 to a perpendicular one like 2 should produce negligible variations in ^2J. This had been verified[18] in the INDO approximation without comment[19] and is supported by experimental evidence to be given below.

Small dependence of ^{2}J *on* π *charges and solvent.* Attention is drawn to the surprisingly small variations of experimental ^2J values in Table 1, as compared to the much wider total range (12 Hz) in Table 2. The spectral representation[20] of the 1,1,2-trimethylallyl cation indicates that ^2J is smaller than the long-range coupling constant (entry 1 of Table 1). Changing the total π charge by two formal units leads to allyl anions[21–25] (entries 2–10) with only modest variation in ^2J, including solvent and cation effects as well as π-allyl bonding in the complex[26] of entry 9. Propene with $^2J = +2.08$ Hz[27] might be considered a reference. A direct comparison was made in entries 11–14 between 1-azaallyl anions and their parent *sec*-enamines;[28] similar behaviour becomes evident from some vinyl ethers[29–31] (entries 15–17) and the enolate[25,32] of entry 18. It would not even be necessary to invoke small π-charge effects because the σ-inductive influence of the charged atoms would operate in the same direction due to reduced electronegativity.

Running through the usual range of π-electron donor and acceptor *p*-substituents in styrene derivatives[33–36] reveals only minor changes of ^2J, as shown in entries 19–21 of Table 2. About the same small variations are observed in entries 22–24 and 25–27 for compounds with

Table 1. Dependence of $^2J(H^A, H^B)$ in allyl-type compounds 1 on substituents R and X. Signs of ^2J determined experimentally, inferred (in parentheses), or unspecified (in slashes)

Entry	R	X	^2J [Hz]	Ion, Solvent	Source
1	CH_3	$\oplus C(CH_3)_2$	|≤1.5|	F_5SbCl^-	ref.[20]
2a	H	$\ominus CH_2$	(+)1.6	Li^+, THF	ref.[21]
2b	H	$\ominus CH_2$	(+)2.8	K^+, Cs^+, THF	ref.[21]
3	H	$\ominus CHCH_3$	(+)3.4	K^+, THF	ref.[21]
4	H	$\ominus CHCH_2tC_4H_9$	(+)1.8	Li^+, THF	ref.[22]
5	H	$\ominus CHC_6H_5$	(+)3.2	Li^+, THF	ref.[23]
6	H	$\ominus C(CH_3)C_6H_5$	(+)3.5	K^+, NH_3	ref.[24]
7a	H	$\ominus C(C_6H_5)_2$	(+)3.6	K^+, NH_3	ref.[24]
7b	H	$\ominus C(C_6H_5)_2$	+3.6	Li^+, THF	ref.[25]
8	CH_3	$\ominus CH_2$	(+)2.9	K^+, THF	ref.[21]
9	CH_3	$\ominus C(CH_3)_2$	ca.(+)2	Pd(II)	ref.[26]
10	CH_3	$\ominus CHC_6H_5$	(+)3.3	K^+, NH_3	ref.[24]
11a	H	$NH\text{-}cC_6H_{11}$	|≤0.3|	THF	ref.[28]
11b	H	$\ominus N\text{-}cC_6H_{11}$	+1.3	Li^+, THF	ref.[28]
12a	C_2H_5	NHC_6H_5	0	THF	ref.[28]
12b	C_2H_5	$\ominus NC_6H_5$	(+)2.3	Li^+, THF	ref.[28]
13a	tC_4H_9	NHC_6H_5	0	THF	ref.[28]
13b	tC_4H_9	$\ominus NC_6H_5$	(+)2.3	Li^+, THF	ref.[28]
14a	C_6H_5	NHC_6H_5	0	THF	ref.[28]
14b	C_6H_5	$\ominus NC_6H_5$	(+)1.4	Li^+, THF	ref.[28]
15	H	O-vinyl	-1.8	CCl_4	ref.[29]
16	H	$O\text{-}iC_4H_9$	-1.7	$Si(CH_3)_4$	ref.[30,31]
17	H	$O\text{-}tC_4H_9$	-0.1	-	ref.[30]
18	H	$\ominus O$	+1.56	Li^+, THF	ref.[25,32]

reduced π-conjugation due to increasing steric hindrance. This suggests that the π-charge alterations caused by the *p*-substituents are sensed at protons H^A and H^B not by π-conjugation but rather via σ-orbitals (if not through space[33]).

Solvent effects on ^2J rarely exceed a ±0.5 Hz variation,[37,38] including even extreme cases.[39] The reaction-field model provides a proper explanation in all cases by modulation of the β-substituent interaction with the CH_2 group.[37,38] Temperature effects on ^2J are extremely rare.[11]

^2J and the σ-inductive effect. If π-interactions are insignificant, can the substituent influence on ^2J be a pure σ-effect? Some further examples[40–55] in Table 2 (entries 28–45) serve to demonstrate the much larger range of ^2J. For most of these substituents one would not expect the operation of a strong π-effect, whereas σ_I constants (if known) bear a certain resemblance to ^2J. Since both ^2J and σ_I are proportional to energies, a linear relation between them might be postulated in a first attempt to deduce new (and desirable pure) inductive σ_I^J constants. To this end, I adopted the policy of choosing some primary substituents (entries 35–42) whose σ_R^0 parameters are known with good precision[3] but of absolute values less than 0.09; that is, simple alkyl groups were excluded. Here and in the sequel the currently acknowledged σ_I data were taken from various compilations.[2,56–59] Although the sequence of substituent effects is of course independent of the choice of the origin, the calibrating substituents in Fig. 1 (filled symbols) define a straight line according to eqn (1) even with the imposed restriction that hydrogen should represent the origin as in most σ scales.

$$\sigma_I^J = 0.15(\pm 0.005) \cdot (2.4 - {}^2J). \qquad (1)$$

It is encouraging to observe that several other substituents (entries 33, 34, 43, 44 and 45), corresponding to the very extremes of known σ_I values, fall close to the line of eqn (1) as shown in Fig. 1 by the open symbols.

Accepting the validity of eqn (1), one may venture to compute new σ_I^J parameters from the preceding and further[60–106] coupling constants of olefin derivatives 1. A large but somewhat contracted series is shown in Table 3 where the entries have been sequenced so as to arrange the key atoms according to groups of the Periodic Table.

Correlation with other observables. The internal CCC

Table 2. Selected $^2J(H^A, H^B)$ values for olefins 1; inferred signs given in parentheses

Entry	R	X	^2J [Hz]	Source
19	H	$C_6H_4NO_2$-(4)	+0.56	ref.[33-35]
20	H	C_6H_5	+1.09	ref.[33-35]
21	H	$C_6H_4N(CH_3)_2$-(4)	+1.25	ref.[33-35]
22	CH_3	$C_6H_4NO_2$-(4)	+1.07	ref.[33,34]
23	CH_3	C_6H_5	+1.62	ref.[33,34,36]
24	CH_3	$C_6H_4N(CH_3)_2$-(4)	+1.74	ref.[33,34]
25	tC_4H_9	$C_6H_4NO_2$-(4)	+1.19	ref.[33,34]
26	tC_4H_9	C_6H_5	+1.79	ref.[33,34]
27	tC_4H_9	$C_6H_4N(CH_3)_2$-(4)	+2.07	ref.[33,34]
28	H	Li (THF)	+7.6	ref.[25,40]
29	H	MgBr (THF)	+7.4	ref.[40,41]
30	CH_3	Li (THF)	(+)7.5	ref.[25]
31	CH_3	Li (Et_2O)	(+)5.4	ref.[25,42]
32	CH_3	MgBr (THF)	(+)6.4	ref.[41]
33	H	$Si(CH_3)_3$	+3.8	ref.[43]
34	H	Sn/4	+3.2	ref.[25,44]
35	H	H	+2.4	ref.[45,46]
36	H	$CH{=}CH_2$	+1.74	ref.[47,48]
37	H	CH_2OH	(+)1.71	ref.[49]
38	H	CH_2Cl	+1.27	ref.[50]
39	H	CH_2Br	+1.20	ref.[50]
40	H	CH_2CN	+1.0	ref.[51]
41	H	$CHCl_2$	+0.26	ref.[52]
42	H	CCl_3	-0.49	ref.[49]
43	H	NO_2	-1.8	ref.[25,49,53]
44	H	$^{\oplus}N(C_2H_5)_2CH_3$	-3.85	ref.[55]
45	H	$^{\oplus}N(CH_3)_3$	-4.25	ref.[54,55]

angle in the benzene nucleus at the point of substituent attachment has recently been claimed to depend predominantly on the σ-inductive effect of the substituent X.[107-109] Figure 2 shows the new σ_I^J constants plotted against such angles[107-121] observed for substituents corresponding to the following entries of Table 3: Entries 46,[108] 49 (X = MgC_6H_5),[110] 51,[111] 54 (X = $B(C_6H_5)_2$ and $B(OH)_2$),[112,107] 55 (X = $Al(C_6H_5)_2$),[107] 56-57,[107] 58,[108,109] 61 (X = $C{\equiv}CC_6H_5$),[113] 62,[108,109] 78,[108,109,114] 103,[108,109,115,116] 105,[109,117] 110,[109] 116,[107,118] 118 (X = $GeO(C_6H_5)_2$),[119] 120 (X = $SnO(C_6H_5)_2$),[119] 123,[108,109] 127 (X = $^{\oplus}NH_3$ and pyridinium),[108,109,120] 129,[109] 130,[108,109,116,121] 131,[107] 132,[107] 136,[107] 137,[107] 139,[108] 140,[108] 150,[107] 152 (X = SO_2CH_3 and $SO_2C_6H_5$),[109,107] 155 (X = $SO_3^{\ominus}$),[109] 158,[107,108] 159[107,108] and 160.[107] Considering the relatively low precision of bond angles from crystal structures, the scatter in Fig. 2 for more than 30 data points is not worse than for 13 points[109] in σ_I correlation. The successful extension of the σ_I^J correlation to organometallic derivatives should be noted; bridging phenyl groups (as in phenyllithium) were excluded from the plot.

Geometry and ^2J are ground state properties; it is hardly surprising that observables involving two different electronic states do not normally correlate with σ_I^J. For example, acid–base equilibria are not dominated by I_σ effects in solution[122] or in the gas phase.[9] Ionization potentials of valence (σ) electrons[123] (even for free radicals[124]) and of core electrons[125] as well as apicophilicities[126] do not run parallel to σ_I^J.

Nuclear quadrupole coupling constants, although a ground state property and claimed[127] to be mainly σ_I-controlled, are recognizably influenced by π-interactions. Electronegativity is a useful but quantitatively not well-defined concept as shown by the divergences between various scales.[128] Many authors have noted a modest relation[89,129,130] with ^2J values; it follows that σ_I^J cannot correlate better. Theoretical values of σ-charge

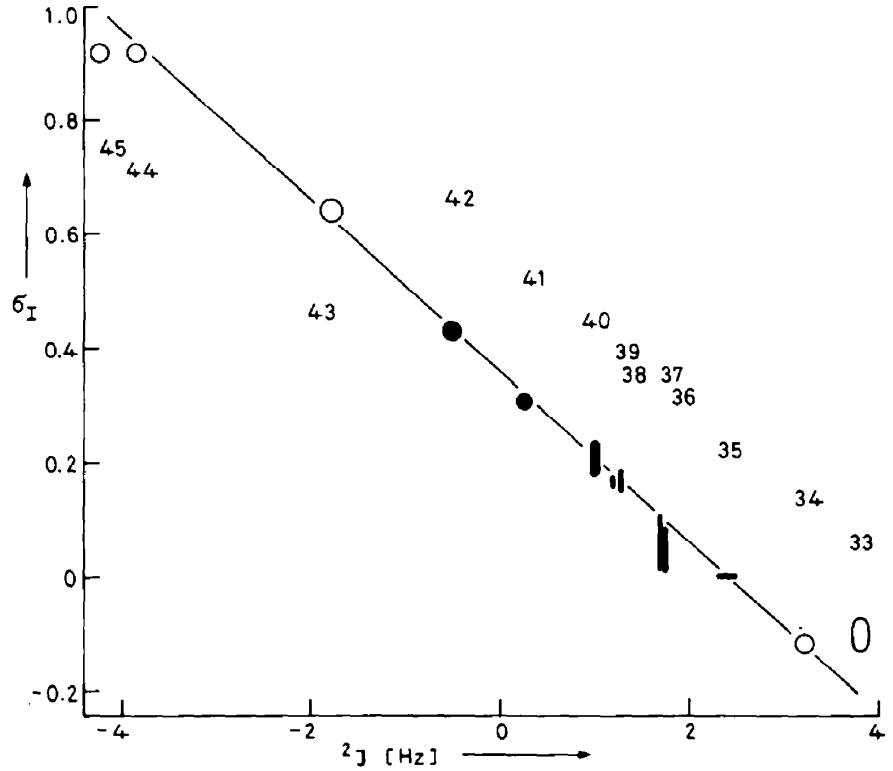

Fig. 1. Selected literature values of σ_I constants as a calibrating function of coupling constants ^2J, with entry numbers from Table 2.

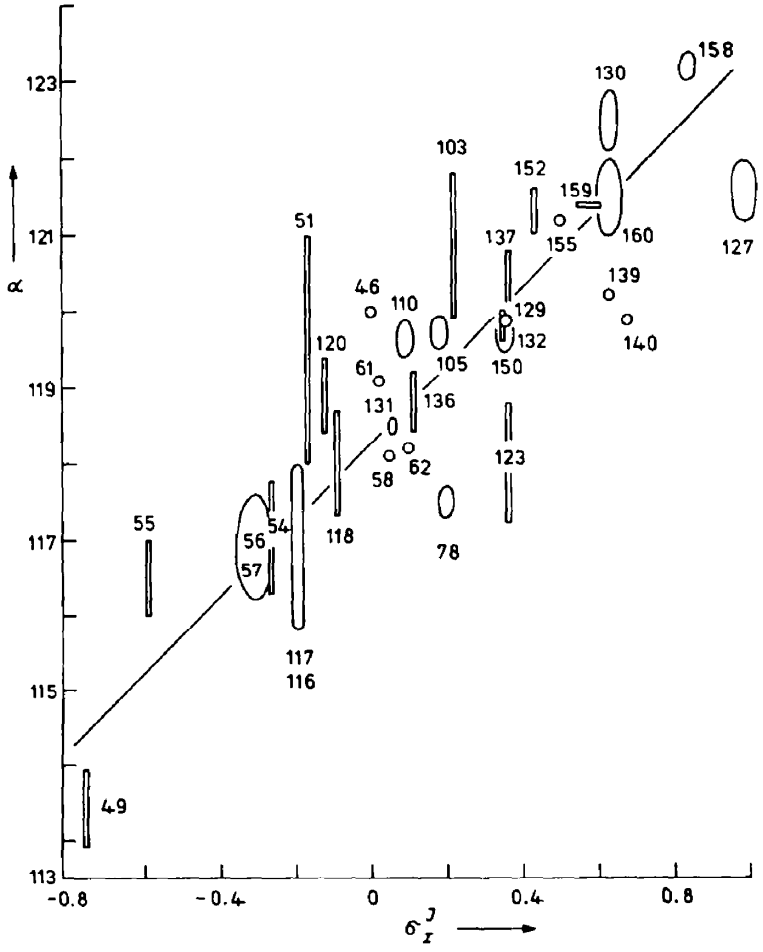

Fig. 2. Intranuclear angles $\alpha(C_2C_1C_6)$, in degrees, of 1-substituted benzenes as a function of σ_I^J.

transfer[131a,b] as "observables" show a reasonable relation to σ_I^J even though the interplay with π-charges must be allowed for.

DISCUSSION

The usual σ_I constants, if used in a dual parameter approach, provide valuable correlations of observables like chemical shifts, equilibria, and reaction rates which depend on differences of electronic energy in two states. That is, σ_I successfully incorporate polarization, electrical field, and hyperconjugation effects.

The σ_I^J parameters derived from ^2J in the single parameter relationship of eqn (1) do not represent another variant to replace old σ_I values but are fundamentally different quantities. They measure the substituent's influence on the electronic ground state directly (analogous to new σ_R^0 values[3]) by a very small perturbation rather than by drastic electrical changes like ionization; the observable is the substituent-modulated magnetic (spin–spin) interaction of hydrogen nuclei with the σ-bonding electrons. The present hypothesis does not imply that π and other effects are unimportant for the magnitude of ^2J; it rather assumes that ^2J differences should prevalently be influenced by differences of σ-inductive β-substituent effects. It is conceivable that other mechanisms contribute and magnify the observable ^2J up to useful sensitivity; they cannot be excluded unless they have structural (e.g. conformational) dependencies different from I_σ. Be this the case or not, applications of σ_I^J to observables containing electronic state changes are likely to meet with failure.

The quality of σ_I^J hinges upon the reliability of ^2J values. Comparing results for the same compounds from different sources, it is not unusual to spot uncertainties of at least ±0.1 Hz, corresponding in favourable cases to $\Delta\sigma_I^J$ *ca.* ±0.02 and sometimes much worse. In order to avoid any bias and to show the necessity for eventual further testing, no selection of literature data was made with respect to experimental quality (or to compatibility with our model).

Since I_σ should be a short-range property related to local charges, one expects the key atoms in β-position to set the scale of σ_I^J. Secondary substituents at the key atom and occasionally also specific solvent effects may cause some variation. A glance at Table 3 verifies these expectations. For example, inspection of CN (σ_I^J = 0.22), NO_2 (0.63), SO_2R (*ca.* 0.45), and OR (*ca.* 0.63) provides a convincing illustration and furthermore demonstrates that electrical dipole moments are not of primary importance since the group moments[132] for the first three substituents are fairly similar but much larger than for the last one. Field effects parameters $\mathcal{F}$[8] correlate poorly with σ_I^J.

A comparison of $\sigma_I^{2,56-59}$ with σ_I^J reveals significant deviations, as expected. The new σ_R^0 parameters[3] (valid for mono-substituted and *meta*-disubstituted benzenes) offer the opportunity of returning to original σ_{meta} data[58] as primary experimental evidence. The difference $\sigma_{meta} - \sigma_R^0$ should[57,133] provide a "corrected" set of polar constants and turns out to be in excellent agreement with the following σ_I^J parameters: Entries 54, 58, 60, 105, 114, 123, 127, 143, 146, 150 and 159–161. In other words, σ_{meta} is efficiently corrected in these cases by σ_R^0 for all those substituent influences which cannot be measured by σ_I^J. Serious increases (> 0.11 σ_I units) are found in σ_I^J for t-butyl (entry 77) and fluoro (158), correspondingly serious reductions for cyano (103), trimethylsilyl (116), oxide (142), sulfoxyl (152) and sulfonyl (152). It is to be noted that σ_I^J, $\sigma_{meta} - \sigma_R^0$, and Grob's[134] parameter σ_I^q, but not σ_I give the same ordering of Br > Cl > I; fluoro appears much more σ-electron attracting if measured by σ_I^J as compared to $\sigma_{meta} - \sigma_R^0$. Cyano falls rather short of the hitherto accepted strong σ-acceptor behaviour; its π-acceptor character may have been underestimated and, indeed, appears somewhat controversial.[3,135,136] Another explanation would assume a field effect contribution to σ_{meta} which does not equally operate in σ_I^J and is not corrected for by σ_R^0. However, trimethylsilyl has also been noted to give unexpected results in the same sense.[137] The negatively charged oxygen (142) in the enolate is seen to act only weakly σ-electron withdrawing, in agreement with *ab initio* calculations.[138]

Me (58) and/or Et (60) groups are stronger σ-acceptors than hydrogen on the σ_I^J, $\sigma_{meta} - \sigma_R^0$, σ_{IB}[136] and σ_I^q scales;[134] theoretical evidence[131b-d] points in the same direction. Neither the "inductive" nor the "Baker–Nathan" order[139] is obeyed in the alkyl sequencing of entries 58, 60, 65, 70 and 77, t-Bu being the strongest σ-acceptor in this series. This reversed order, compared to the σ_I sequence,[56] is not necessarily incompatible with suggestion[4] that alkyl induction and polarization have very nearly the same structural dependencies. However, molecular polarizability[5,6] can hardly be responsible for the positive σ_I^J values since there is no net electrical charge to be stabilized in **1**.

The apparently strong σ-acceptor character of the transition metal complexes in entries 63, 79, 141, 145 and 148 had been supported by a ^2J sign determination only in the first case; it is furthermore uncertain whether these moieties can still be regarded as β-substituents. The synthetically valuable, high nucleofugicity of imidazolyl-(1) in acylation reactions[140] is seen from entry 128 to parallel its strong σ-acceptance, comparable to chloro (entry 159).

Hybridization has been suggested[141] as a factor in addition to electronegativity determining ^2J. Some of the very few estimations of the terminal CH_2 angles indicate quite similar values (*ca.* 120°) for the vinyl halides.[142] The large change of σ_I^J towards ethylene (angle *ca.* 118°)[143] and the smaller further change towards trivinylborane (angle 104°)[144] also suggest that hybridization is an inferior factor. This CH_2 compression by electron releasing β-substituents is borne out by calculations on the vinyl anion.[145] Since the corresponding increase of ^2J is completely contrary to the angular dependence which was repeatedly[18,141] predicted by the otherwise successful theoretical[18] treatment, we conclude that hybridization effects are overrun by substituent influences also in the computational approach.

NMR coupling constants are generally dominated by the Fermi contact mechanism and hence *a priori* dependent on σ-electron densities.[29,146] Therefore, a rough correlation of $^2J_{HH}$ with other types of coupling constants like $^2J_{CH}$[147] is often found, and a higher electronegativity of alkyl than of hydrogen may be inferred.[148]

CONCLUSION

Theoretical and experimental considerations suggest a single-parameter eqn (1) as a first approximation to quantify σ-inductive effects I_σ. It is recognized that experimental and interpretative refinements of this simplistic approach may be inevitable. If subsequent progress corroborates the proposal, $^2J_{HH}$ may turn out to be

Table 3. σ_I^J values of substituents X in 1, as computed from eqn (1). [a] v = vinyl, [b] cycloocta-1,3,5,7-tetraen-1-yl, [c] or +0.21 for ^2J = +1 Hz, [d] and anthr-1-yl, [e] and phenanthr-9-yl, pyren-1-yl, chrysen-6-yl, [f] isocyanide and its Co(III) complex, [g] if ^2J negative, [h] (±0.02), [i] (±0.03), [k] (±0.05)

Entry	X in 1 (R = H)[a]	σ_I^J	Source of ^2J	Entry	X in 1 (R = H)[a]	σ_I^J	Source of ^2J
46	H	0	ref.[45,46]	104	$C(OCH_3)CH_2$	+0.08	ref.[47]
47	Li(THF)	-0.78	ref.[25,40]	105	CO-nAlk	+0.18	ref.[25,80a,83]
48	$Li(Et_2O)$	-0.71	ref.[60,61]	106	$COCH=CH_2$	+0.15	ref.[49,83]
49	MgBr	-0.75	ref.[40,41]	107	COC_6H_5	+0.01	ref.[83]
50	MgCl	-0.76	ref.[41,61]	108	$COC(CH_3)_3$	-0.01	ref.[83]
51	Hg-v	-0.17	ref.[62]	109	$CONR^1_2$	ca.-0.13	ref.[49]
52	$HgOOCCH_3$	-0.09	ref.[63a]	110	CO_2Alk, CO_2H	ca.+0.09	ref.[49,80b]
53	HgBr	ca.-0.05	ref.[63a]	111	CO_2CO-v, COF	ca.+0.24	ref.[49,85]
54	Bv_2	-0.26	ref.[63b]	112	furyl-(2)	+0.15	ref.[84]
55	Alv_2	-0.59	ref.[62]	113	thienyl-(2)	+0.24	ref.[84]
56	Gav_2	-0.26	ref.[64]	114	CF_3, COCl	+0.33	ref.[78,49]
57	$Ga(CH_3)_2$	-0.35	ref.[64]	115	CCl_3	+0.43	ref.[49]
58	CH_3	+0.05	ref.[27]	116	$Si(CH_3)_3$	-0.20	ref.[43,86]
59	CH_2K	-0.08	ref.[21]	117	Siv_3, $Si(aryl)_3$	-0.18	ref.[80a,81,49,86,87]
60	C_2H_5	+0.07	ref.[27]	118	Gev_3, Ge_2v_5	-0.09	ref.[49,87]
61	$C\equiv CCH_3$	ca.+0.02	ref.[65]	119	$Ge(C_6H_5)_3$, $SnClR^1_2$	0	ref.[49,87]
62	$CH=CH_2$	+0.10	ref.[47,48]	120	Snv_3, $Sn(C_6H_5)_3$	-0.12	ref.[25,44,62,87,88]
63	$CH=CH_2/Fe(CO)_3$	+0.72	ref.[66]	121	PbR^1_3	+0.06	ref.[49,87]
64	$CR^1=CHR^2$	+0.06	ref.[47,48]	122	$\oplus_{NR^1}$	+0.17	ref.[28]
65	n-Alk	ca.+0.03	ref.[27,49]	123	NHR^1, NR^1_2	+0.36	ref.[28,49,89]
66	$CH_2CH(CH_3)_2$	+0.05	ref.[67]	124	carbazolyl-(9)	+0.48	ref.[25,49]
67	$CH_2C(CH_3)_3$	0	ref.[67]	125	NC [f]	+0.43	ref.[90]
68	$CH_2CH=CH_2$	+0.07	ref.[68]	126	NCO	+0.38	ref.[49]
69	$CH_2C_6H_5$	+0.08	ref.[50]	127	$\oplus N(CH_3)_3$	+1.00	ref.[54,55]
70	$CH(CH_3)_2$	+0.10	ref.[67]	128	imidazolyl-(1)	+0.60	ref.[25,49,91]
71	$CH(t\text{-}C_4H_9)_2$	-0.03	ref.[67]	129	NR^1COR^2, $N(COR^1)_2$	+0.36	ref.[25,49,74,90]

73	c-$C_3H_4R^1$	ca.+0.12	ref.[70,71]
74	c-C_6H_{11}	+0.07	ref.[49]
75	c-C_6H_9-(1)	+0.15	ref.[49]
76	c-C_8H_7 [b]	+0.16	ref.[49]
77	$C(CH_3)_3$	+0.15	ref.[25,72]
78	C_6H_5	+0.20	ref.[33-35]
79	$C_6H_5/Cr(CO)_3$ [c]	ca.+0.51	ref.[73]
80	C_6H_4Hal-(2)	+0.20	ref.[35]
81	C_6H_4Alk-(2)	ca.+0.12	ref.[35]
82	$C_6H_3Alk_2$-(2,6)	ca.+0.03	ref.[25,35]
83	$C_6H_2(CH_3)_3$-(2,4,6)	+0.02	ref.[35,74]
84	anthryl-(2)	ca.+0.36	ref.[75]
85	naphthyl-(1)	ca.+0.21	ref.[75]
86	naphthyl-(2) [d]	ca.+0.14	ref.[75]
87	anthryl-(9) [e]	ca.+0.06	ref.[75]
88	pyridyl-(2)	+0.11	ref.[76]
89	pyridyl-(3)	+0.22	ref.[76]
90	pyridyl-(4)	+0.24	ref.[76]
91	$CH_2Sn(CH_2CH{=}CH_2)_3$	+0.06	ref.[44]
92	CH_2CN	ca.+0.21	ref.[51]
93	CH_2NH_2	ca.+0.08	ref.[49,77]
94	CH_2NO_2	+0.25	ref.[53b]
95	CH_2OH	+0.10	ref.[49]
96	CH_2OCH_3	+0.06	ref.[52]
97	CH_2F	+0.13	ref.[78]
98	CH_2Cl, CH_2Br, CH_2I	+0.18	ref.[50,52]
99	CHO	+0.21	ref.[79]
100	$CH(OCH_3)_2$	+0.08	ref.[52]
101	CHF_2	+0.26	ref.[78]
102	$CHCl_2$	+0.32	ref.[52]
103	CN	+0.22	ref.[29,37,80b-82]
131	Pv_2, PR_2^1	+0.06	ref.[49,92]
132	$\oplus P(C_2H_5)_3$	+0.35	ref.[92]
133	$P(O)R_2^1$, $P(S)R_2^1$	+0.11	ref.[49,93]
134	$PO(OC_2H_5)_2$	+0.02	ref.[92,94]
135	PCl_2, PBr_2, $PSCl_2$	+0.32	ref.[49]
136	Asv_2, AsR_2^1	+0.11	ref.[49]
137	$\oplus As(C_6H_5)_3$	+0.36	ref.[95]
138	Sbv_2	+0.05	ref.[49]
139	OH [g], OC_2H_5, OC_4H_9	+0.63	ref.[96,30,31,49,25]
140	OCH_3	+0.68	ref.[29-31,97]
141	OCH_2CF_3, $OH/Fe(CO)_4$	+0.81 [g]	ref.[96b,98]
142	OLi	+0.13	ref.[25,32]
143	$OCHR_2^1$, Oaryl	ca.+0.57	ref.[49,99]
144	$OSi(CH_3)_3$	ca.+0.36	ref.[98]
145	$OSi(CH_3)_3/Fe(CO)_4$	+0.81 [g]	ref.[98]
146	OOCH, $OOCR^1$	+0.60	ref.[100,74,49]
147	$OOCSC_6H_5$, $OOCNHR^1$	+0.51 [g]	ref.[101]
148	$OOCNHCH_3/Fe(CO)_4$	+0.96 [g]	ref.[98]
149	$OPO(OR^1)_2$	+0.71	ref.[49]
150	SR^1, $S(C_6H_5)$=Naryl	+0.36	ref.[25,49,102,103]
151	$SC(CH_3)_3$	+0.20	ref.[25,102]
152	$S(O)CH_3$, SO_2R^1	+0.43	ref.[49,25]
153	SO_2-v, $SO_2C_4F_9$	+0.48	ref.[104,25]
154	$SO_2NR_2^1$	+0.39	ref.[49]
155	SO_3H	+0.5	ref.[105]
156	SO_2OR^1	+0.47	ref.[49]
157	SF_5	+0.42 [g]	ref.[106]
158	F	+0.84 [h]	ref.[29,37,49,99]
159	Cl	+0.58 [i]	ref.[29,37,49,99]
160	Br	+0.63 [i]	ref.[29,37,49,99]
161	I	+0.54 [k]	ref.[37,49,99]

one of the very few observables which measure I_σ correctly. Its use is restricted to terminal olefinic derivatives 1 (as opposed to ketenes and cumulenes) but applicable to most or all β-substituents.

EXPERIMENTAL

The ^{1}H NMR spectra of several compounds have been checked for the sign of the olefinic $^2J_{HH}$ coupling constants by INDOR[149] experiments with the added advantage of assigning hidden spectral lines.[150] Computer simulations of the vinyl spectral parts (60 MHz) served to confirm the analyses; numbers in parentheses indicate the uncertainties in the last digit. Anhydrous diethyl ether and THF were distilled from Na/benzophenone.

1,1-Diphenylallyllithium. Entry 7[b] (R. Lehmann). 1,1-Diphenylpropene, too weakly acidic to react with lithium diisopropylamide, was quickly deprotonated by 1-phenylvinyllithium[151] in [D$_8$]THF. ^{1}H NMR spectral parameters equalled those of the potassium salt in ammonia,[24] except for olefinic $^3J_{cis}$ = 10.9 Hz; ^2J = +3.6 Hz by INDOR.

2-Lithio-propene. Entries 30 and 31 (Dr. E. Lattke). 2-Bromopropene was prepared[152] from 2-methylpropenoic acid and had b.p. 46.5–48° (Lit.[152] 47–49°). The lithium compound in diethyl ether was obtained by 2 h stirring with Li ribbon; ^{1}H NMR agreed with lit.[42]

The solvents were removed at 0.01 Torr and the residue dissolved in THF to give a stable soln. ^{1}H NMR δ 5.92 and 5.02 (2 dq, ^2J = 7.5, ^4J = 1.5). No spectral changes occurred upon cooling to −62° in both solvents.

Vinyllithium. Entries 28 and 47 (Dr. E. Lattke). From tetravinyltin[153] and BuLi in pentane,[60] evaporated and redissolved in [D$_8$]THF; ^{1}H NMR (simulated) δ 7.249(1) (H − 1), 6.664(1) (H − 2, *trans*), 5.921(1) (H − 2, *cis*), ^2J = +7.56(9), ^3J = +18.81(9) and +23.98(9); no spectral change at −47°. Solns in diethyl ether and in C_6D_6 with 10% of THF showed identical distances within each multiplet.

3,3-Dimethyl-1-butene. Entry 77. ^{1}H NMR[72] verified with ^2J = +1.37 by INDOR.

2',6'-Dimethylstyrene. Entry 82 (Dr. E. Lattke). ^2J = +2.4 by INDOR.

2-Vinylpyridine. Entry 88. ^2J = +1.66 (courtesy of Prof. T. Schaefer).

Buten-3-one. Entry 105. ^{1}H NMR (CCl$_4$) δ 6.263(5) (H − 2), 6.129(4) (H − 1, *cis*), 5.827(2) (H − 1, *trans*), ^3J = +17.4(2) and +10.7(2), ^2J = +1.2(2).

Tetravinyltin. Entries 34 and 120 (R. Mertz, R. Lehmann). B.p. 72°/38 Torr (Lit.[153] 67–70°/28 Torr), ^2J = +3.2(1) verified by INDOR (Lit.[62] 3.7, Lit.[44] + 3.14).

N-Vinylcarbazole. Entry 124 (P. Löw). ^{1}H NMR (CCl$_4$) δ 7.095(2) (H − 1), 5.730(2) (H − 2, *cis*), 4.941(2) (H − 2, *trans*), ^3J = + 15.7(2) and 9.3(2), ^2J = − 0.8(1).

N-Vinylimidazole. Entry 128 (P. Löw). ^{1}H NMR (CCl$_4$) δ 6.887(1) (H − 1), 5.181(1) (H − 2, *cis*), 4.7165(9) (H − 2, *trans*), ^2J = −1.58(7), ^3J = +9.13(8) and +15.82(8).

N-Vinyl-2-pyrrolidone and N-acetyl-N-vinylaniline. Entry 129. ^{1}H NMR (CCl$_4$) ^2J < 0.3.

Nitroethene. Entries 43 and 130 (Dr. P. Dvortsák, E. Räpple). Prepared from 2-nitroethanol and phthalic anhydride.[154] A relatively well-resolved ^{1}H NMR spectrum could be obtained in $DCCl_3$ to solve the peculiar discrepancies of the literature data[49,53] by INDOR: ^2J = −1.8.

Butyloxy-ethene. Entry 139, ^2J = −1.8 by INDOR and simulation.

Lithium ethanolate. Entries 18 and 142 (P. Löw). ^{1}H NMR[32] verified except for positive ^2J by INDOR.

Propylthio-ethene. Entry 150 (H. Graf, R. Brückner). ^{1}H NMR (CCl$_4$) δ 6.229(2) (H − 1), 5.077(1) (H − 2, *trans*), 4.974(1) (H − 2, *cis*), ^3J = +10.1(1) and +16.5(1), ^2J = −0.0(1).

Phenylthioethene. Entry 150 (H. Graf, R. Brückner). ^{1}H NMR (CCl$_4$) δ 6.425(2) (H − 1), 5.234(2) (H − 2, *trans*), 5.221(2) (H − 2, *cis*), ^3J = +16.7(2) and +9.6(2), ^2J = +0.0(2) by INDOR (compare Ref. [102]).

t-Butylthio-ethene. Entry 151 (H. Graf, R. Brückner). ^{1}H NMR[102] (CCl$_4$) verified with ^3J = +1.1(2) by INDOR.

Phenylsulfonyl-ethene. Entry 152 (M. Fahimi). ^{1}H NMR (CCl$_4$) δ 6.640(2) (H − 1), 6.412(2) (H − 2, *cis*), 6.003(1) (H − 2, *trans*), ^3J = +16.6(1) and +10.0(1), ^2J = −0.4(1).

Nonafluorobutylsulfonyl-ethene. Entry 153 (Dr. K. Laping). ^{1}H NMR ([D$_6$]benzene) δ 6.022(2) (H − 2, *cis*), 5.837(1) (H − 1, long-range coupling to ^{19}F), 5.329(1) (H − 2, *trans*), ^3J = 16.48(8) and 9.8(2), ^2J = −0.8(3); ^{1}H NMR[155] (CCl$_4$) δ 6.7 (m).

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