CALCULATION OF ONE BOND C,C COUPLING CONSTANTS AS A PRODUCT OF TWO EMPIRICAL STRUCTURE-RELIED FACTORS[1]

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Summary

Empirical factors I(C) have been evaluated from experimental $^1J(C,C)$ data for a variety of structural fragments. It is also shown how I(C) factors can be obtained from $^1J(C,H)$ or from Malinowski's ζ increments. The product of such I(C) values reproduces $^1J(C,C)$ for very different combinations of carbon fragments.

As a consequence of a steady improvement in C-13 NMR instrumentation and of the use of labelled substrates in mechanistic and biosynthetic studies there has been an increasing interest in the determination, interpretation and structural application of C,C coupling constants. The rather large values of $^1J(C,C)$ are of particular interest since they are now more easily obtained, even from non-labelled substrates. Quantumchemical calculations[2] have shown that in many cases this interaction is dominated by the Fermi contact term, which is reflected in the concept of s character of the bonding hybrid orbitals Since such calculations are cumbersome and the results depend upon the method employed, this approach is not of much practical use, if one is interested to make an estimate of $^1J(C,C)$ for any given C,C fragment in a larger molecule.

It is, however, conceivable to represent $^1J(C,C)$ as the product of two empirical factors $I(C_1)$ and $I(C_2)$:

$$^1J(C_1,C_2) = I(C_1) \cdot I(C_2) \text{ [Hz]}$$

These factors, according to the equation of McConnell,[3] would include elements of the respective s electron density, of the C,C bond order and of the singlet-triplet excitation energy. In order to derive I(C) values from experimental coupling constants it is useful to define four key factors which can be obtained from the corresponding symmetrical molecules (Table 1) and characterize the fragments $-CH_3$, $=CH_2$, $=CH-$(arom), and $\equiv CH$.

Table 1. Key Factors I(C) [$Hz^{1/2}$] from Symmetrical Molecules

Substance	$^1J(C,C)$ exp.[a][Hz]	Moiety	Ref.	I(C) [$Hz^{1/2}$]
H_3C-CH_3	34.6 ± 0.1	$-CH_3$	4a,b	5.88 ± 0.01
$H_2C=CH_2$	67.6 ± 0.2	$=CH_2$	4a,d	8.22 ± 0.01
benzene	55.8 ± 0.5	$=C-(Ar)$	4c,d	7.47 ± 0.03
$HC\equiv CH$	172.0 ± 1.0	$\equiv CH$	4a,d	13.11 ± 0.04

[a] For comparison, a set of calculated[2c] Fermi-contact contributions to $^1J(C,C)$ is: 34.45 Hz, 68.27 Hz, 63.13 Hz, 136.14 Hz, respectively.

With the aid of these key factors, further I(C) values can be obtained from unsymmetrical molecules of any kind by dividing the experimental C,C coupling constant by the corresponding key factor. In this way I(C) values for a variety of structural fragments have been derived from methyl substituted compounds (Tables 2-5). I(C) values for cycloalkanes are also evaluated and listed in Table 5. The data for three-, four- and five-membered rings demonstrate ring strain effects on I(C) and illustrate that the parameters obtained from unstrained systems are not applicable to small rings.

Table 2. $^1J(C,C)$, $^1J(C,H)$, and Calc. I(C) Values for the Systems CH_3-CXYZ and H-CXYZ

X	Y	Z	$^1J(C,C)$ [Hz] (exp.)	Ref.	I(C) [± 0.05 $Hz^{1/2}$]	$^1J(C,H)$ [Hz] (exp.)
H	H	OCH_2CH_3	38.9 ± 0.1	5a	6.62	-
H	H	F	38.2 ± 0.1	5a	6.50	141.1
H	H	OH	37.7 ± 0.1	5a,b,2a	6.41	141.0
H	H	NH_2	35.8 ± 0.1	5a	6.09	133.0
H	H	COOH	34.8 ± 0.1	5a	5.92	130.0
H	H	H	34.6 ± 0.1	4a,b	5.88	125.0
H	H	CH_2OH	34.2 ± 0.5	2a,5b	5.82 ± 0.1	126.9
H	H	C_6H_5	34 ± 2	5c	5.80 ± 0.3	129.4
H	H	CH_3	33 ± 2	5a	5.60 ± 0.3	124.9
H	CH_3	OH	38.4 ± 0.8	2a,5b	6.53 ± 0.2	140.3
CH_3	CH_3	Br	40.2	5d	6.84	-
CH_3	CH_3	OH	39.5 ± 0.8	2a,5b	6.72 ± 0.2	142.8
CH_3	CH_3	CH_3	35.5 ± 0.1	4d	6.28	-

Table 3. Systems CH_3-X and H-X

X	$^1J(C,C)$ [Hz] (exp.)	Ref.	I(C) [$\pm$ 0.05 Hz$^{1/2}$]	$^1J(C,H)$ [Hz] (exp.)
$CH{=}CH_2$	41.9 $\pm$ 0.1	5g	7.13	156.2
C_6H_5	44.2 $\pm$ 0.15	5f	7.57	159
$C{\equiv}CH$	67.4 $\pm$ 0.1	5g	11.46	249

Table 4. Systems CH_3-COX and H-COX

X	$^1J(C,C)$ [Hz] (exp.)	Ref.	I(C) [$\pm$ 0.05 Hz$^{1/2}$]	$^1J(C,H)$ [Hz] (exp.)
OC_2H_5	58.8 $\pm$ 0.1	5e	10.00	225.6
OH	56.7 $\pm$ 0.1	2a,5e	9.64	222.0
Cl	56.1 $\pm$ 0.1	5e	9.54	-
$N(CH_3)_2$	52.2 $\pm$ 0.1	2a,5e	8.88	191.2
C_6H_5	43.3 $\pm$ 0.1	5c,e	7.36	173.7
CH_3	40.4 $\pm$ 0.1	2a,5b	6.87	172.4
H	39.4 $\pm$ 0.2	2a,5e	6.70	172.0

Table 5. Exp. $^1J(C,C)$, $^1J(C,H)$ and Calc. I(C) Values for Methyl-cycloalkanes

$^1J(2,1)$[$\pm$ 0.1 Hz]	44.0[5b]	36.1[4d,5h]	36.2[4d]	35.7[4d]	35.4[4d]
$^1J(2,3)$[$\pm$ 0.1 Hz]	13.4[4d]	28.9[4d,5h]	-	33.3[4d]	34.9[4d]
$^1J(2,H)$[Hz]	160 $\pm$ 2	136 $\pm$ 1	131 $\pm$ 2	127 $\pm$ 2	-
I(2→1)[Hz$^{1/2}$]	7.5 $\pm$ 0.1	6.15 $\pm$ 0.1	6.15 $\pm$ 0.1	6.1 $\pm$ 0.1	6.0 $\pm$ 0.1
I(3→2)[Hz$^{1/2}$]	3.7 $\pm$ 0.1	5.4 $\pm$ 0.1	-	5.8 $\pm$ 0.1	5.9 $\pm$ 0.1

It has been demonstrated[5b] that there is a linear correlation between $^1J(\underline{C},\underline{C}H_3)$ and the corresponding $^1J(C,H)$ coupling constants. Similarly, I(C) can be correlated with $^1J(C,H)$ (Table 2, compare also Tables 3-4):

$$I(C) = 45.5 \cdot 10^{-3} \cdot {}^1J(C,H) \ [Hz^{1/2}]$$

Furthermore, since $^1J(C,H)$ can be calculated from additive substituent incre-
ments[7] ζ it is conceivable to apply a similar approach to the calculation of
I(C) for the fragment C(X,Y,Z) from empirical increments $\chi(X)$, $\chi(Y)$, $\chi(Z)$.
The χ values can be obtained either from a set of I(C) values (Table 2) or
via the following correlation between χ and ζ :

$$\chi = 45.5 \cdot 10^{-3} \cdot \zeta \quad [Hz^{1/2}]$$

In this way I(C) values can be composed for combinations of substituents X, Y
and Z not contained in Table 2.

The calculation of $^1J(C,C)$ coupling constants from I(C) values leads to a
satisfactory agreement with experimental data for a large variety of structur-
al systems. In particular, coupling constants in sp^3-sp^3 and sp^3-sp^2 frag-
ments can be reproduced with typical deviations of less than $\pm$ 1 Hz. In sp^2-
sp^2 fragments it appears that the deviations increase with the extent of con-
jugation which is not accounted for in the I(C) factors. In such cases the
deviations may be as large as $\pm$ 3 Hz. Poor agreement is observed for C,C
bonds containing one or two sp carbon atoms. This behaviour is not unexpected
since the Fermi contact contribution to $^1J(C,C)$ of the C,C triple bond is
known to be only 80% (Table 1).

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