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THE PREDICTION OF ^{29}Si–H AND ^{13}C–H COUPLING CONSTANTS IN SUBSTITUTED SILANES AND METHANES

M. A. JENSEN
The Chemical Laboratory, University of Sussex, Falmer, Brighton (Great Britain)

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In a recently published paper[1] we have used the Pople–Santry method[2] of calculating coupling constants in a study of substituent effects on directly bonded ^{29}Si–H and ^{13}C–H couplings. The calculations which we have made account for the quadratic nature of the additive substituent effects in silanes[3] and methanes[4] in terms of one parameter α_X for each substituent X. It was shown that the M–H coupling constant $J(\mathrm{MHXYZ})$ in MHXYZ (M = ^{29}Si, ^{13}C) can be expressed:

$$J(\mathrm{MHXYZ}) = J(\mathrm{MH_4}) + A\cdot(\alpha_X+\alpha_Y+\alpha_Z) + B\cdot(\alpha_X^2+\alpha_Y^2+\alpha_Z^2) + C\cdot(\alpha_X\cdot\alpha_Y+\alpha_Y\cdot\alpha_Z+\alpha_Z\cdot\alpha_X) \qquad (1)$$

For silanes the constants A, B and C were found to have the values:

$$A = 18.26 \text{ cps/eV} \quad B = 1.78 \text{ cps/eV}^2 \quad C = -2.98 \text{ cps/eV}^2$$

whereas for methanes the values are:

$$A = -8.28 \text{ cps/eV} \quad B = -0.21 \text{ cps/eV}^2 \quad C = 0.78 \text{ cps/eV}^2$$

The value of α_X—the Coulomb integral or effective electronegativity of the group X—can be determined, using eqn. (1), from the M–H coupling in any X–M–H fragment. The coupling in MHXYZ can be used to determine α_X, provided α_Y and α_Z are already known. In the simplest case, α_X can be calculated from the coupling observed in $\mathrm{MH_3X}$. Eqn. (1) then reduces to:

$$J(\mathrm{MH_3X}) = J(\mathrm{MH_4}) + A\cdot\alpha_X + B\cdot\alpha_X^2 \qquad (2)$$

the value of α_X falling within the range −4 to 1 eV.

If the coupling is known for either of the compounds $\mathrm{MH_2X_2}$ or $\mathrm{MHX_3}$, the appropriate eqns. are:

$$J(\mathrm{MH_2X_2}) = J(\mathrm{MH_4}) + 2A\cdot\alpha_X + (2B+C)\cdot\alpha_X^2 \qquad (3)$$

and

$$J(\mathrm{MHX_3}) = J(\mathrm{MH_4}) + 3A\cdot\alpha_X + (3B+3C)\cdot\alpha_X^2 \qquad (4)$$

It is clear that slightly different values of α_X will be found from the couplings in each X-substituted silane or methane which may be chosen for a calculation based on eqn. (1). To avoid ambiguities of this nature, it is possible to consider any or all of the available couplings in X-substituted compounds. α_X may be adjusted to give the best possible "least-squares" fit to these measurements. We have found that the most convenient compromise, between choosing one compound arbitrarily and using all the available measurements, is to consider the couplings in MH_3X, MH_2X_2 and MHX_3. α_X is chosen to give the best fit to these couplings, using eqns. (2), (3) and

TABLE 1

VALUES OF α_X FOR VARIOUS SUBSTITUENTS X IN SILANES AND METHANES (in eV)

X	α_X[a]		*X*	α_X[a]
	Silanes	*Methanes*		*Silanes*
F	−2.67	−3.57	$OSiH_3$	−1.76
Cl	−2.50	−2.88	NMe_2	−0.51
Br	−2.53	−2.83	Ph	0.10
I	−2.04	−2.93[b]	Me	0.36
OMe	−1.49	−2.13		

[a] α_X is chosen to give the best fit to the couplings in MH_3X, MH_2X_2 and MHX_3. [b] Chosen to fit the couplings in CH_3I and CH_2I_2 only, since the coupling in CHI_3 has not yet been reported.

TABLE 2

PREDICTED AND OBSERVED COUPLINGS $J(^{29}Si–H)$ IN SILANES (in cps)

Compound	*J(predicted)*[a]	*J(observed)*	*Source*
SiH_4	−202.5	−202.5	5
SiH_3F	−238.5	−229.0	5
SiH_2F_2	−295.9	−282	5
$SiHF_3$	−374.4	−381.7	5
SiH_3Cl	−237.0	−238.1	5
SiH_2Cl_2	−290.2	−288.0	5
$SiHCl_3$	−362.1	−362.9	5
SiH_3Br	−237.2	−240.5	5
SiH_2Br_2	−291.0	−289.0	5
$SiHBr_3$	−363.7	−358.2	[b]
SiH_3I	−232.3	−240.1	5
SiH_2I_2	−274.6	−280.5	5
$SiHI_3$	−329.3	−325.1	6
$SiH_3(OMe)$	−225.7	−216.2	7
$SiH_2(OMe)_2$	−255.5	−247.6	6
$SiH(OMe)_3$	−291.7	−297.9	6
$SiH_3(OSiH_3)$	−229.2	−221.5	5
$SiH_2(OSiH_3)_2$	−265.1	−256.6	6
$SiH(OSiH_3)_3$	−310.3	−316.0	6
$SiH_3(NMe_2)$	−211.3	−205.7	6
$SiH_2(NMe_2)_2$	−221.0	−217.6	6
$SiH(NMe_2)_3$	−231.3	−235	6
SiH_3Ph	−200.6	−199.4	[b]
SiH_2Ph_2	−198.7	−197.6	[b]
$SiHPh_3$	−196.9	−198.0	[b]
SiH_3Me	−195.6	−194.2	8
SiH_2Me_2	−189.1	−188.6	9
$SiHMe_3$	−183.0	−184.0	9

[a] Predictions based on eqn. (1), with α_X values from Table 1. [b] Present work.

(4). The values which we have found in this way for nine common substituents in silanes, and five in methanes, are shown in Table 1.

Tables 2 and 3 show the observed and calculated couplings in the mono-, di-, and trisubstituted silanes and methanes which were used to determine the α_X values given in Table 1.

TABLE 3

PREDICTED AND OBSERVED COUPLINGS $J(^{13}C–H)$ IN METHANES (in cps)

Compound	*J(predicted)*[a]	*J(observed)*[b]
CH_4	125	125
CH_3F	152	149
CH_2F_2	189	185
CHF_3	236	238
CH_3Cl	147	150
CH_2Cl_2	176	178
$CHCl_3$	211	209
CH_3Br	147	152
CH_2Br_2	175	178
$CHBr_3$	209	206
CH_3I	148	151
CH_2I_2	177	173
CHI_3	213	
$CH_3(OMe)$	142	140
$CH_2(OMe)_2$	162	162
$CH(OMe)_3$	186	186

[a] Predictions based on eqn. 1, with α_X values from Table 1. [b] Experimental measurements from ref. 6

α_X values which have been calculated by the method outlined above, or, less reliably, by using the coupling in a single X–M–H fragment, may be used to predict the couplings in other compounds. The values of α_X etc. are substituted into the general eqn. (1). α_H is, of course, zero. In order to test the accuracy of prediction which is to be found when the α_X values have been determined by the method suggested here, we have calculated M–H couplings for compounds containing more than one of the types of substituent listed in Table 1. Since the discrepancies between prediction and observation are generally larger for silanes than for methanes (compare Tables 2 and 3), we have chosen to study the results for silanes over a series of twenty compounds, but those for methanes over only four compounds. The prediction of the silane couplings is a rigorous test of the method. The calculated and observed couplings for silanes are shown in Table 4, and those for methanes in Table 5.

The standard deviation between prediction and observation (making no allowance for experimental error) in Table 4 is 2.3%. This is a satisfactory result for a method based on a coupling constant calculation which, apart from other drastic assumptions, considers only the Fermi contact term contribution to the coupling.

The effect of a β substituent (one atom removed from the M–H fragment in which the coupling is measured) is smaller than the effect of a similar α substituent. Even so, the effect may be significantly larger than the errors in prediction mentioned above. We have therefore studied the couplings in some X methyl silanes, and have

TABLE 4

PREDICTED AND OBSERVED COUPLINGS $J(^{29}Si-H)$ IN SILANES WITH MORE THAN ONE TYPE OF SUBSTITUENT (in cps)

Compound	*J(predicted)*[a]	*J(observed)*	*Source*
SiH_2FMe	−228.8	−222.3	8
$SiHFMe_2$	−219.4	−215.8	10
$SiHF_2Me$	−283.2	−273.1	10
SiH_2ClPh	−234.4	−236.5	[b]
SiH_2ClMe	−227.5	−229.0	8
$SiHClPh_2$	−231.8	−235.1	[b]
$SiHClMe_2$	−218.3	−222.3	[b]
$SiHClPhMe$	−224.9	−229.2	[b]
$SiHCl_2Ph$	−286.8	−288.5	[b]
$SiHCl_2Me$	−288.0	−279.5	[b]
SiH_2BrPh	−234.6	−235.6	[b]
SiH_2BrMe	−227.6	−231.1	8
$SiHBrMe_2$	−218.4	−225.0	10
$SiHBr_2Me$	−278.7	−280.8	10
SiH_2IMe	−223.3	−231.0	8
$SiHIMe_2$	−214.6	−224.8	10
$SiHI_2Me$	−263.3	−271.6	10
SiH_2PhMe	−193.8	−193.0	[b]
$SiHPhMe_2$	−187.4	−188.0	[b]
$SiHPh_2Me$	−192.0	−194.0	[b]

[a] α_X values from Table 1. [b] Present work.

TABLE 5

PREDICTED AND OBSERVED COUPLINGS $J(^{13}C-H)$ IN METHANES WITH MORE THAN ONE TYPE OF SUBSTITUENT (in cps)

Compound	*J(predicted)*[a]	*J(observed)*	*Source*
$CHCl_2F$	219	220	11
$CHClF_2$	227	231	11
CH_2BrCl	175	179	12
CH_2BrI	176	176	12

[a] α_X values from Table 1.

TABLE 6

CALCULATED AND OBSERVED COUPLINGS $J(^{29}Si-H)$ IN SOME METHYL SILANES (in cps)

Compound	*J(predicted)*[a]	*J(observed)*[b]
$ClCH_2SiH_2Me$	−198.8	−198.5
Cl_2CHSiH_2Me	−208.6	−208.2
$BrCH_2SiHMe_2$	−192.9	−193.2
ICH_2SiHMe_2	−191.0	−191.4
$(CH_3CH_2)_3SiH$	−178.8	−179.2

[a] Eqn. 5 was used to caculate the effect of the β substituents. [b] Source: present work.

found that the effect of a β substituent X on the ^{29}Si–H coupling can be written:

$$\delta(\beta\text{-X}) = K \cdot \alpha_X \tag{5}$$

where $K = 3.9$ cps/eV. The value of $\delta(\beta\text{-X})$ is added to the coupling calculated without considering the β substituent. Good agreement with the observed couplings is achieved, as can be seen from an inspection of Table 6.

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SUMMARY

The effect of substituents on directly bonded ^{29}Si–H and ^{13}C–H coupling constants is discussed. The effect of a substituent X is characterised by a parameter α_X, a Coulomb integral or electronegativity. The relationship between α_X and the coupling constant in an X-substituted silane or methane has been calculated by the Pople–Santry method. The determination of α_X values is discussed. Values of α_X for nine substituents in silanes, and five in methanes are presented. The effects of β substituents on ^{29}Si–H couplings is described. ^{29}Si–H and ^{13}C–H couplings are calculated for more than seventy silanes and methanes, and the results are compared with the observed couplings.

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