

# The $^{13}\text{C},\text{H}$ Coupling Constants in Structural and Conformational Analysis. Part I. The Correlation of $^2J(\text{CH}_3\text{CH})$ and $^2J(\text{HCH})$ in Certain Systems

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The geminal  $^2J(\text{CH}_3\text{CH})$  coupling constants were determined for a number of cyclic compounds. A linear correlation was found to exist between the corresponding  $^2J(\text{HCH})$  and  $^2J(\text{CH}_3\text{CH})$ , the expression for the correlation being determined as  $^2J_{\text{CH}} = 0.55 \times ^2J_{\text{HH}} + 4.93$  from regression analysis. A correlation of the same linear type was detected also for those unsaturated acyclic compounds where the methyl group is attached to an  $sp^2$  carbon, the correlation being here expressed as  $^2J_{\text{CH}} = 0.58 \times ^2J_{\text{HH}} + 2.86$ . The restrictions of these correlations are also discussed.

The coupling constants between directly and indirectly bonded protons and carbon-13 have been studied by many authors.<sup>1-4</sup> The results indicate a clear relation to a number of structural and atomic properties of the compounds, such as bond lengths and angles, electronegativities of substituents, hybridization of the coupled atoms and additivity of substituent effects. It has also been noted that in general a linear relation exists between the corresponding  $J_{\text{CH}}$  and  $J_{\text{HH}}$  (and likewise between  $J_{\text{CH}}$  and  $J_{\text{CC}}$ ), the ratio  $J_{\text{CH}}/J_{\text{HH}}$  being +0.4 to +0.7.<sup>1-4</sup> As pointed out earlier, one should determine  $J_{\text{CC}}$  and  $J_{\text{CH}}$  values of a system that can be related to a geometrically equivalent carbon-proton or proton-proton system, respectively.<sup>3,4</sup>

The present article is concerned with the two-bond coupling constants in systems where a hydrogen is being replaced by a methyl group and a comparison between  $^2J_{\text{HH}}$  and  $^2J_{\text{CH}}$  in the same geometrical surroundings is possible.

## EXPERIMENTAL

All carbon data were measured with a JEOL FX-60 instrument at 15.04 MHz. The spectra were taken from concentrated samples (20–50 % w/v) in acetone- $d_6$  or in deuteriochloroform. A spectrum width of 500–1000 Hz was used in the observation of the non-decoupled methyl carbons and the data capacity was 8K. A proper  $S/N$  ratio was achieved in general by 1000–5000 accumulations. A gated decoupling technique (with NOE) was used to enhance the  $S/N$  ratio. The experimental error in the values of  $^2J_{\text{CH}}$  couplings is considered to be  $\pm 0.1$  Hz in most cases. The compounds under examination were chosen as to allow a first order analysis of the spectra. In some cases (*cf.* below) first order methods are not strictly applicable but due to large relative chemical shifts of the protons (more than 6 times the corresponding  $J$ 's in each case) the probable additional inaccuracy in some values is less than  $\pm 0.1$  Hz.

## RESULTS

The data from the following cyclic compounds are collected in Table 1: 2-methyl-2-*tert*-butyl-4,6-dioxo-1,3-dioxane (1), *trans*-2,5-dimethyl-2-*tert*-butyl-4,6-dioxo-1,3-dioxane (2), 2-phenyl-4,6-dioxo-1,3-dioxane (3), *cis*-2-phenyl-5-methyl-4,6-dioxo-1,3-dioxane (4), 6-methyl-2-oxo-1,4-dioxane (5), *trans*-3,6-dimethyl-2-oxo-1,4-dioxane (6), *cis*-3,6-dimethyl-2-oxo-1,4-dioxane (7), 6-methyl-4-oxo-1,3-dioxane (8), *trans*-5,6-dimethyl-4-oxo-1,3-dioxane (9), 3,4-dihydro-2,3-dimethyl-2*H*-1,3-benzoxazine (10), 3,4-dihydro-*cis*-2,3,4-trimethyl-2*H*-1,3-benzoxazine (11), 3,4-dihydro-*trans*-2,3,4-trimethyl-2*H*-1,3-benzoxazine (12), *cis*-3,5-dimethyl-2-

Table 1. Observed geminal  $J(HCH)$  and  $J(CH_3CH)$  in the studied compounds.

Compound	Carbon	$^2J(HCH)$	Ref.	Compound	$^2J(CH_3CH)$
1	5	-21.4	14	2	-6.2
3	5	-18.5	14	4	-5.4
5	3	-17.7	15	6	-4.3
5	3	-17.7	15	7 <sup>a</sup>	-4.2
8	5	-17.6	16	9	-4.6
10	4	-16.6	17	11 <sup>a,b</sup>	-4.6
10	4	-16.6	17	12 <sup>b</sup>	-4.7
6	5	-12.5	15	14	-2.3
15	6	-12.0	16	18	-2.4
19	6	-10.9	18	9	-1.3
13	6	-10.9	15	14	-1.6
16	2	-10.4	17	11 <sup>a,b</sup>	$\begin{cases}  J  < 1.5^c \\  J  < 1.5^c \\  J  < 0.5^c \end{cases}$
16	2	-10.4	17	12 <sup>b</sup>	
17	2	-9 <sup>d</sup>	7	23 <sup>b</sup>	
20	2	-6.1 <sup>d</sup>	7	21	+1.6
22	2	-5.4	19	18	+2.3
24	2	+1 <sup>d</sup>	7	25	+6.0

<sup>a</sup> Axial methyl group (at least partially). <sup>b</sup> The average orientation of the N-CH<sub>3</sub> group may be different from that of the reference compound. This can affect the relation of  $^2J_{HH}$  and  $^2J_{HC}$  (see Refs. 6-8). <sup>c</sup> Unresolved signals due to other small long range couplings. These values were omitted from the regression analysis. <sup>d</sup> A "best value", see Refs. 6-7.

oxo-1,4-dioxane (13), *trans*-5,6-dimethyl-2-oxo-1,4-dioxane (14), 2,5,5-trimethyl-4-oxo-1,3-dioxane (15), 3,4-dihydro-3,4-dimethyl-2*H*-1,3-benzoxazine (16), tetrahydro-3-methyl-1,3-oxazine (17), *cis*-2,5,5,6-tetramethyl-4-oxo-1,3-dioxane (18), 5-methyl-4-oxo-1,3-dioxane (19), 1,3-dioxane (20), 2-methyl-1,3-dioxane (21), 5,5,6-trimethyl-4-oxo-1,3-dioxane (22), tetrahydro-2,3-dimethyl-1,3-oxazine (23), 1,3-dioxolane (24), 2-methyl-1,3-dioxolane (25).

The <sup>1</sup>H data were taken from reported results in the literature. Some of them are collected from unpublished works from this laboratory. As mentioned above the compounds were selected to allow a first order analysis of the carbon-13 spectrum; the methyl group is generally located on a carbon being situated between two hetero atoms or two fully substituted carbons (or carbonyls). Thus in most cases there are only two observable couplings in the CH<sub>3</sub> signal, a large  $^1J_{CH}$  and the much smaller  $^2J_{CH}$ , both of which can directly be measured.

It is known that several factors influence the  $^2J_{HH}$  value in cyclic and acyclic systems;<sup>8-9</sup> the interference by these factors was removed by a suitable choice of compounds, bearing

in mind that the ring geometry should not change due to the substitution of a hydrogen by a methyl group. In most cases the reference compounds for <sup>1</sup>H data were selected so that only the methyl group under study was replaced by a hydrogen. In some cases this was not possible and another type of reference compound to give  $^2J_{HH}$  was used (cf. Table 1). This may cause a minor inconsistency between the corresponding  $^2J_{HH}$  and  $^2J_{CH}$  values due to reasons mentioned above.

It is known that  $^2J_{HH}$  can be of either sign, a negative one being more usual in *sp*<sup>3</sup> CH<sub>2</sub> groups. The  $^2J_{HH}$  of methane is -12.4 Hz,<sup>10</sup> which corresponds to a negative  $^2J_{CH}$  in ethane.<sup>11</sup> Thus it is obvious that a  $^2J_{CH}$  associated with a large negative  $^2J_{HH}$  also is negative. It is also obvious that at a certain value of  $^2J_{HH}$  the corresponding  $^2J_{CH}$  coupling becomes positive because large positive  $^2J_{HH}$  couplings are associated with a large positive  $^2J_{CH}$  coupling, e.g. formaldehyde (+41 Hz)<sup>12</sup> vs. acetaldehyde (+26.7 Hz).<sup>13</sup> From Table 1 it is seen that the absolute value of  $^2J_{CH}$  becomes gradually smaller as the absolute value of the corresponding  $^2J_{HH}$  decreases but begins to increase again as  $^2J_{HH}$  goes from ca. -6 Hz

Table 2. Values of  ${}^2J(\text{HCH})$  and  ${}^2J(\text{CH}_2\text{CH})$  over  $sp^2$  carbons.  ${}^2J(\text{CH}_2\text{CH})$  values predicted from eqn. (1) are also shown.

Compound	${}^2J_{\text{HH}}$	${}^2J_{\text{CH}}$		Ref.
		obs.	pred.	
Formaldehyde	+41	—	—	12
Acetaldehyde	—	+26.7	+27.5	13
3,5-Dinitrophenylhydrazone of formaldehyde	+11.6	—	—	20
of acetaldehyde	—	+9.1	+11.3	This work
Acrylic acid	+1.7	—	—	21
Crotonic acid	—	+3.9	+5.9	This work
Propenal	+1.0	—	—	22
<i>trans</i> -2-Butenal	—	+3.5	+5.5	This work
Acrylonitrile	+0.9	—	—	23
<i>trans</i> -Crotonitrile	—	+3.5	+5.4	This work
<i>cis</i> -Crotonitrile	—	+3.5	+5.4	This work

to *ca.* 0 Hz. Hence the  ${}^2J_{\text{CH}}$  coupling must change sign somewhere around  ${}^2J_{\text{HH}} = -9$  Hz.

As a first try, we have applied a linear regression analysis to the data of Table 1. This seems to be a rather good approximation since the correlation coefficient appears to be 0.991 suggesting, indeed, an approximately linear correlation:

$${}^2J_{\text{CH}} = 0.551 (\pm 0.020) \times {}^2J_{\text{HH}} + 4.929 (\pm 0.292) \quad (1)$$

Eqn. (1) may be tested for, *e.g.*, formaldehyde and acetaldehyde, by substituting  ${}^2J_{\text{HH}} = +41$  Hz<sup>12</sup> which gives  ${}^2J_{\text{CH}} = +27.5$  Hz which fits well with observed value (26.7 Hz). However, the validity of eqn. (1) for these  $sp^2$  carbon compounds is slightly fortuitous since in other  $sp^2$  carbon compounds (Table 2) the agreement between the values of  ${}^2J_{\text{HA}}$  and  ${}^2J_{\text{CH}}$  is not as good as for formaldehyde *vs.* acetaldehyde. In fact, the examples of Table 2 subjected to a regression analysis yield another linear correlation (correlation coefficient 1.000):

$${}^2J_{\text{CH}} = 0.578 (\pm 0.006) \times {}^2J_{\text{HH}} + 2.863 (\pm 0.111) \quad (2)$$

The slope of eqn. (2) is nearly the same as in eqn. (1) but the intercept is somewhat smaller.

## CONCLUSIONS

The present study indicates that a linear correlation exists between corresponding  ${}^2J_{\text{CH}}$  and  ${}^2J_{\text{HH}}$  in similar geometrical surroundings,

as could be anticipated from earlier results.<sup>1-4</sup> A behaviour like this is reasonable if the coupling mechanisms are similar, *i.e.* dominated by the Fermi contact term.

A relation between  ${}^2J(\text{HCH})$  and  ${}^2J(\text{CH}_2\text{CH})$  can be used to solve many kinds of problems. First, the  ${}^2J_{\text{CH}}$  value of a methyl group in a compound having several different  $\text{CHCH}_2$  fragments may be used as an aid in the spectral analysis: the corresponding  ${}^2J_{\text{HH}}$  can usually be estimated (if it is not known) from known correlations with structure of this coupling constant,<sup>5-8</sup> and through eqn. (1) can the corresponding  ${}^2J(\text{CH}_2\text{H})$  coupling be calculated with a reasonable accuracy and can be compared with the observed coupling. A second application is to use the relation in conformational analysis because the  ${}^2J_{\text{HH}}$  and  ${}^2J_{\text{CH}}$  seem to behave similarly in a conformational sense. Finally, eqns. (1) and (2) provide a way to establish the signs of  ${}^2J(\text{CH}_2\text{CH})$  couplings provided the corresponding  ${}^2J(\text{HCH})$  is known and that the value of  ${}^2J_{\text{CH}}$  is not too close to zero (or  ${}^2J_{\text{HH}}$  too close to *ca.* -9 Hz).

It should be noted that the above correlations are limited to such systems where the central carbon is a part of a 5- or 6-membered (or larger) ring or an  $sp^2$  carbon. Thus, for example, in the three-membered ring of propylene oxide, the predicted value of  ${}^2J(\text{CH}_2\text{CH})$  is +8.0 Hz<sup>24</sup> from eqn. (1) (and +6.1 Hz from eqn. 2), while the observed value is *ca.* +7 Hz (being between the values calculated for  $sp^2$  and  $sp^3$  carbons). Similarly, eqn. (1)

is not suitable for aliphatic acyclic compounds of the mono- or disubstituted ethane type; for example, the  $^2J_{\text{HH}}$  of methane is  $-12.4 \text{ Hz}$ <sup>9,10</sup> and the predicted value of  $^2J_{\text{CH}}$  in ethane is  $-1.9 \text{ Hz}$ , well removed from the observed coupling of  $-4.5 \text{ Hz}$ .<sup>11</sup> Clearly, another type of correlation must be sought for these types of compounds.

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