NMR-EXPERIMENTS ON ACETALS—PART 32

DEPENDENCY OF GEMINAL COUPLING CONSTANTS OF METHYLENE GROUPS ON ELECTRONEGATIVITY, BOND LENGTH AND FREE ORBITAL OVERLAP OF ADJACENT LOBES
AN EMPIRICAL RELATIONSHIP AS A TOOL FOR CONFORMATIONAL DESCRIPTION

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Abstract—An equation, obtained by iterative fitting of experimental data in some 1,3-diheterocyclic, monocyclic and alicyclic compounds, is proposed. This enables prediction of $^2J(XCH_2Y)$ as depending on three main contributions: the Pauling electronegativities of X and Y, the bond distances C—X and C—Y and the mutual orientation of the free orbitals and $\sigma(CH)$ bonds. For the reading of the quantitative contribution to ^2J by the latter phenomenon (p–σ "parallelity effect") a monogram is presented allowing prediction of the geminal coupling values and conformational discussions in (X,Y-dihetero) cyclic compounds with X and/or Y = S, O, Se, C.

INTRODUCTION

It has previously been suggested from experimental data,[1] that when a p-orbital of an α-O or α-N atom in X—CH$_2$ moieties is parallel with an adjacent σ-CH-bond, the geminal coupling constant $^2J(CH_2)$ increases by about $+1.8$ cps. As ^2J is usually negative (except in small rings) the result is a decrease in its absolute value. The proposed increment was said to be realised after a correction was made for an "intrinsic" electronegativity-contribution by the adjacent hetero-atom. This conclusion has also been reached by Crabb *et al.*[4] who showed the effects of α-hetero-atoms on ^2J.[2-6] We report here that in heterocyclic and acyclic compounds the ^2J can be predicted with fairly good approximation, taking three contribution factors into consideration: (a) the electronegativity, (b) the bond lengths d(C—X) and (C—Y) with respect to the XCH$_2$Y moieties and finally, (c) an even more important dependency of ^2J on the mutual spacial orientation between the adjacent p-free electron orbitals of X and Y and the (C—H)σ-bonds under consideration. Thus the observation of the geminal coupling values of XCH$_2$Y may give important quantitative information about conformation of the system.[7,9]

DISCUSSION

In predicting correct ^2J values for CH$_2$ groups, flanked by hetero-atoms or carbon atoms in their sp^3 state, several factors might be taken into account: (a) the s-character of the CH$_2$-part (b) the valence angle H—C—H; (c) the spatial orientation of β-substituents;[10,11] (d) the mutual spatial orientation of p-lobes of the α-hetero-atom with

the σ(C—H) bonds under consideration; (e) the nature of the α-hetero-atom ("electro-negativity" and/or other factors, *vide infra*).

The division is only for convenience. Thus, either rule (a) or (b) may be applied, depending whether one knows $^2J(^{13}C$—H$)$ (which can be used as a measure of the s-character)[12] or alternatively the exact value of the valence angle H—C—H may be available from crystallographic data.[13]

With respect to this, sometimes a quite satisfying dependency of $^2J(CH_2)$ and $^2J(^{13}C$—H$)$ may be found.[8] Though the electronegativity of substitution causes a change in hybridization (thus affecting the s-character), one might think that (a) and (e) and also (d) cover a common behaviour. With respect to the contributions mentioned under (d) however, a mechanism is operating that is different for (a). In several compounds, where only the p–σ "parallelity" is greatly changed. Sometimes one notices large changes in $^2J(CH_2)$ but not in $^2J(^{13}C$—H$)$. Thus $^2J(^{13}C$—H$)$ is almost identical in 1,3-dioxolanes (163–167 cps with $^2J(OCH_2O) = 0/ + 1$ cps,[14]) 1,3-dioxanes (164 cps; $^2J(OCH_2O) = -6.2$ cps) or 1,3,5-trioxane (166 cps; $^2J(OCH_2O)$ $= -6.0$ cps). Although the observed difference in ^2J is due to a difference in M.O.-p–σ-overlap, this is thus not reflected in the corresponding $^2J(C^{13}$—H$)$ values.

Point (c) has been illustrated several times,[5] and although not very well known, the effect is not large. Slightly "too negative" values for $^2J(CH_2)$ in (cyclic) compounds may be the result of the occurrence of an anti periplanar electronegative β-substituent. This will only occur if the substituent, carrying free orbitals, is in an axial position or alternatively is situated in the ring. Thus slightly "too negative" values for CH$_2$-–5 in 1,3-dioxanes and other systems, (− 13·6–14 cps; for cyclohexane − 13·0 cps*) may be explained in this light.

We now discuss on a quantitive basis the most important contributing factors (apart form valence angle changes), the "electronegativity" the "bond distance" and the "parallelity"-effect.

Failure of electronegativity-effect as the sole contribution to fluctuations in $^2J(CH_2)$

Cookson and Crabb[4] have proposed† a linear relationship between the sum of Pauling-electronegativities of adjacent (hetero)atoms in XCH$_2$Y moieties and $^2J(CH_2)$ in heterocyclic six- and five-membered rings respectively. In Fig. 1 we have redrawn their proposed relationship (solid line), but apart from the originally chosen model compounds, we have included acyclic models and several dithianes, thioxanes and selenanes etc. ... Also the value (− 13·0 cps) for cyclohexane and related (C—CH$_2$ —C)-moieties have been added.

It is clear that the regression line[4] is a bad one in several aspects. Firstly there is no apparent reason why five membered rings (cfr. no 1) should be excluded and that a different correlation should exist,[4] except for the reason that other factors intervene,

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* Values for $^2J(CH_2)$ in cyclohexane were obtained in d$_8$-cyclohexane (− 12·6 cps),[15] 3,4,5-d$_6$-cyclo-hexanol (− 12·20 cps;[16] OH-essentially equatorial!), *cis, cis,*-1,3,5-tripyridyl-cyclohexane (− 12·50 cps),[17] 3,5-d$_4$-1,1-diMe-cyclohexane (− 13·0 cps at − 80°)[18] and *trans*-1,3-dihalo-1,4-d$_3$-cyclohexanes (− 11 to − 12 cps).[19]

† In a recent paper however they have stressed[6] upon the important influence of suitable orientated lone-pairs, as one of us did originally.[1]
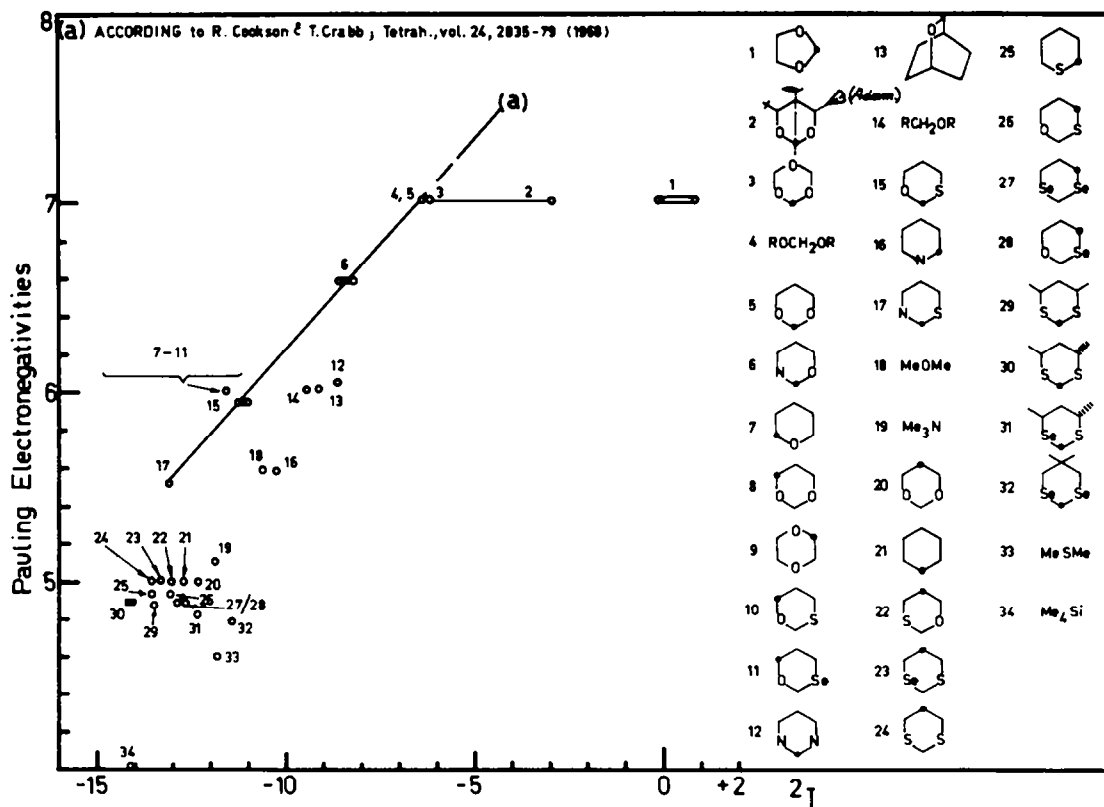
FIG 1. Observed ^2J-values and Pauling's electronegativities. Solid line illustrates earlier proposed linear relationship.[4]

as has been recognised, at least qualitatively,[7,9,6] as being a result of the p–σ parallelity-effect.[1] Apparently it accounts also for the deviation of some hexacyclic derivatives for which the main conformation differs from the chair form (e.g. no. 2,13[7,9]). This may also be the reason why acyclic compounds (no. 14, 18, 33) do not lie on the original regression line.

But this alone cannot be the sole reason for the bad correlation with electronegativity. The proposed relationship becomes even worse on trying to include 1,3-dithianes, 1,3-diselenanes (or their combinations) as seen in no. 29–32. The trend in replacing S for Se results even in a regression line with an opposite slope with respect to the original one, and despite the almost identical electronegativity of S and Se (2·44 and 2·48 resp. in the Pauling scale), $^2J(XCH_2Y)$ differs quite sensitively (= −14·5 and = −11·5 cps resp.) This behaviour may be illustrated in the way, as proposed very recently by Sternhell et al.[8] for ^2J in Me_nX derivatives. Here ^2J was correlated against the period of the heteroelement. It is found that an element of the second period systematically gives pronounced negative contributions to ^2J of the neighbour

CH_2 (Fig. 2). In the 1,3-dihetero-hexacyclic systems this behaviour is identical.* Once again it is instructive to remark that in Me_nX the electronegativity of C and Si differs greatly, causing apparently a shift in ^2J-values, but that an opposite shift is found when changing Si for Sn, although the electronegativity remains almost unchanged (1·74 and 1·72 resp.).

The periodicity in ^2J is not unexpected, for it reflects partly the increasing changes in free orbital localization, (hybridization).

When trying to unify the data, it becomes clear that electronegativity alone does not suffice. Only a little success might be obtained in relating influences by hetero-atoms belonging to the same row in the periodic table.
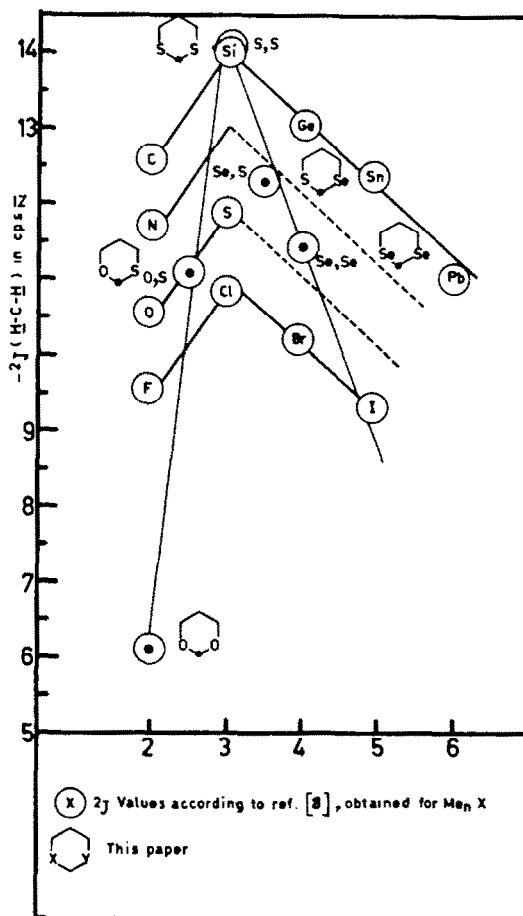

FIG 2. Geminal coupling values in Me_nX[8] and in 1,3-diheterocyclanes as a function of the period of the heteroatoms.

* Sternhell et al.[8] stress upon the pecularity that the periodic correlation results in parallel lines for elements belonging to different columns. As a general behaviour, one might predict for 1,3-disila-cyclohexanes an exceptionally high value for $^2J(SiCH_2Si)$ of $= -21$ cps (cf. $J(OCH_2O) \rightarrow {}^2J(SCH_2S)$ $= -8$ cps; $^2J(SiCH_2Si) = {}^2J(CCH_2C) -8$ cps).

It seems therefore worthy to seek for a correlation between $^2J(XCH_2Y)$, the electronegativity of both X and Y and something which measures the possibilities (intensities) of overlap between the p lobes and adjacent (C—H) bonds, accounting for the specificity of the heteroatom involved. A parameter such as bond distance seems attractive. This has also been proposed very recently by Sternhell[8] who introduced with relative success a correlation between $^2J(Me_nX)$ and the product of electronegativity and bond distance. In the series of heterocyclic compounds we have chosen models for which ideal chair forms were tentatively accepted. Fig. 3 illustrates how the scattering of $^2J(XCH_2Y)$ reported against Pauling electronegativity is much reduced when bond-distance dependency is introduced. For this, several possible empirical relations were tried to fit the experimental data, by means of iterative computation (PDP-8/1 computer with 8K memory).

We will come back to several other trials which were also tested, after we have discussed the introduction of other parameters (such as p–σ and σ–σ torsion relationships). This allowed us to judge the efficiency of the proposed correlations better, as more models could be involved. The best correlation (also used in Fig. 3) was the one
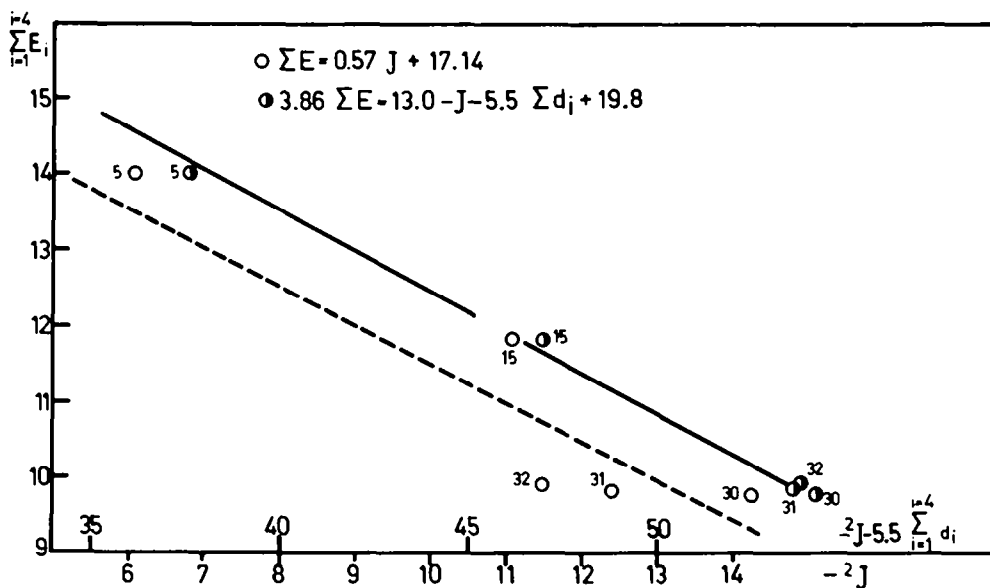

FIG 3. Relationship between electronegativity and ^2J in some selected heterocyclic compounds, before (dotted line and O) and after (full line and ◑) the introduction of the bond distance parameter.

where a linear correction was allowed for both, bond distance and electronegativity, having the expression (A), when the model compounds as indicated in table 1 were taken.

$$^2J = -13.0 + 5.5 \sum_{i=1}^{n} d_i + 3.86 \sum_{i=1}^{n} E_i - 19.8n \text{ (in cps)} \tag{A}$$

Here -13.0 was deliberately taken. in order to be able to refer to cyclohexane. The number of free orbitals is n.* If some N-containing models were included, the best correlation was found to correspond with other coefficients, as illustrated in Table 1.

TABLE 1. COMPARISON OF CALCULATED AND OBSERVED $^2J(XCH_2Y)$ VALUES FOR 1,3-DIHETERO-CYCLANES, USING RELATIONS (A) (N-HETEROCYCLES EXCLUDED) RESP. (B) (N-HETEROCYCLES INCLUDED). ELECTRO-NEGATIVITY ACCORDING TO PAULING-SCALE[a]

(A)	$^2J = -13.0 + 5.5 \sum\limits_{i=1}^{4} d_i + 3.86 \sum\limits_{i=1}^{4} E_i - 19.8 \times 4$ (in cps)					
Comp. no[b]	5	15	21	29, 30	31	32
E_i	3·50	3·50	(2·50)	2·44	2·48	2·48
		2·44			2·44	
d_i (m Å)	1·43	1·43	(1·54)	1·82	1·82	1·93
		1·82			1·93	
$^2J_{ob}$	−6·2	−11·1	−13·0	−14·2	−12·3	−11·5
$^2J_{calc}$	−6·4	−10·5	−13·0[c]	−14·3	−12·8	−11·3

(B)	$^2J = -13.0 + 2.14 \sum\limits_{i=1}^{4} d_i + 2.56 \sum\limits_{i=1}^{4} E_i - 10.23 \times 4$ (in cps)								
Comp. no[b]	5	6	12	15	17	21	29, 30	31	32
E_i	3·50	3·50	3·07	3·50	3·07	(2·50)	2·44	2·48	2·48
		3·07		2·44	2·44			2·44	
d_i (in Å)	1·43	1·43	1·47	1·43	1·47	(1·54)	1·82	1·82	1·93
		1·47		1·82	1·82			1·93	
$^2J_{ob}$	−6·2	−8·0	−8·5	−11·1	−13·0	−13·0[c]	−14·2	−12·3	−11·5
$^2J_{calc}$	−6·1	−8·1	−10·1	−9·8	−11·9	−13·0	−13·6	−12·9	−12·2

[a] The use of other electronegativity scales, such as those of Dailey[21] or Muller[22] gives no satisfying or even coflicting results.

[b] Numbering refers to structures as indicated in Fig. 1.

[c] Reference; here n = 0, thus $^2J = -13.0$ by definition.

$^2J(XCH_2Y)$ and torsional relation between p–orbitals and σ–bonds

As already argued we expect a pronounced influence from the mutual orientation of the p-orbitals and σ-bonds in the X—CH$_2$—Y moiety of cyclic compounds. This indeed has been shown to be the case.[7] In contrast with cookson and Crabb,[4] we have not excluded the five membered ring compounds, but in the first trial we have included only those derivatives for which X = Y = O.

The function fitting best the experimental data in the case of cyclic compounds containing OCH$_2$O moieties, contains the square of a sine function of τ, which is defined by the angle between the line bisecting both C—H bonds and each p-orbital

* For convenience, bond distance as well as electronegativity are summed over the total number of adjacent free p-orbitals; two for each heteroatom. In this case N was also considered as having two p-orbitals, which in fact is not correct·

respectively (total number is 4). For the models mentioned in Table 2 (see also Chart I), the best correlation was computed as:

$$^2J(\tau) = -6.54 + 4.86 \sum_{i=1}^{4} \sin^2 \tau_i \text{ (in cps)} \tag{C}$$

In the light of the foregoing idealization of the conformations, for which ring torsional angles were accepted to be as for idealized carbocyclic derivatives (see Bucourt notations[20] in Chart I), the correlation may be regarded as more than satisfactorily.
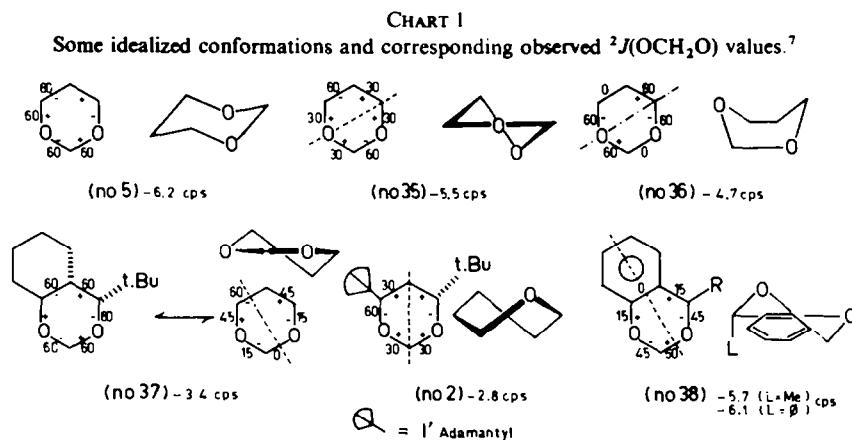
TABLE 2. COMPARISON OF THE OBSERVED AND CALCULATED $^2J(XCH_2Y)$ VALUES FOR SOME SELECTED 1,3-DIOXA-CYCLANES OF APPROXIMATE AND IDEALIZED CONFORMATIONS, ACCORDING TO THE BEST FITTING EQUATION (C)

Comp. no[a]	5	35	36	2	1[b]
τ[b]	0,0	0,30	0,60	30,90	60,60
	120,120	120,90	120,60	30,90	60,60
$^2J_{ob}$[c]	−6.2	−5.5	−4.7	−2.8	+1.0
$^2J_{cal.}$	−7.28	−4.85	−3.64	−2.42	+0.005

[a] Numbering refers to structures as shown in Fig. 1 and/or Chart I, where some of these are symbolized under Bucourt notation.[20]
[b] τ defined as the dihydral angle formed between the line bisecting the $\sigma(C—H)$ bonds of the CH_2 and the p-orbitals of the O.
[c] These values were taken from ref. 7, except for no. 1 (see ref.)[14]

CHART I
Some idealized conformations and corresponding observed $^2J(OCH_2O)$ values.[7]

(no 5) −6.2 cps   (no 35) −5.5 cps   (no 36) −4.7 cps

(no 37) −3.4 cps   (no 2) −2.8 cps   (no 38) −5.7 (L=Me) cps
                                                         −6.1 (L=Ø) cps

⬡ = 1' Adamantyl

Correlation including electronegativity, bond distance and torsional relations

This check consisted in correlating the geminal coupling constants and all foregoing parameters with the aid of a wide variety of heterocycles. The best fitting

equation, including the model compounds indicated in Table 3 was computed to be the expression (D).

$$^2J(d_i, E_i, \tau_1, x) = -13 + 2.35 \sum_{i=1}^{4} d_i + 2.63 \sum_{i=1}^{4} E_i$$

$$+ 4.77 \sum_{i=1}^{4} (x \sin^2 \tau_{1,i} + (1-x) \sin^2 \tau_{2,i}) - 4 \times 12.93 \qquad (D)$$

The possibility to work with heterogeneous conformational mixtures, where x is the molfraction ($x = 1$ for models in Table 3), is included. Here again the value of -13.0 cps was deliberately taken as a point of reference, although it is possible that for $C-CH_2-C$ moieties too, the expression might be adopted. Also N-containing derivatives could be involved. It remains however a point of discussion[27] what are

TABLE 3. COMPARISON OF OBSERVED AND CALCULATED $^2J(XCH_2Y)$ VALUES FOR SELECTED 1,3-DIETHETERO-CYCLANES, ACCORDING TO THE BEST FITTING EQUATION (D), INCLUDING DEPENDENCY WITH ELELCTRO-NEGATIVITY, BOND DISTANCE AND p-σ TORSIONAL SPATIAL ORIENTATION. TRIALS TO FIT WITH EQUATION (G) ARE ALSO INCLUDED FOR COMPARISON.

No[a]	1	2	5	15	21	29	31	32	35	36
$^2J_{ob}$	0/+1	−2.8	−6.2	−11.1	−13.0	−14.2	−12.3	−11.5	−5.5	−4.7
$^2J_{calc}$[b]	0	−2.4	−7.2	−11.3	−13.0	−13.9	−12.6	−11.3	−4.8	−3.6
$^2J_{cal}$[c]	−0.3	−2.7	−7.5	−12.0	−13.0	−15.0	−11.9	−8.8	−5.1	−3.9

[a] Same as in Table 2
[b] According equation (D)
[c] According equation (G)

the populations of the conformations with respectively axial and equatorial lone pairs, and therefore we have to wait for more experimental values.[6]

In order to include monoheterocyclic derivatives (containing $X-CH_2-C$ moieties) we finally added to our expression possible σ–σ torsional contribution factors. We fitted the final equation (H) for determination of the best coefficients for a set of compounds as indicated in Table 4.

$$^2J = 2.19 \sum_{i=1}^{4} d_i + 2.52 \sum_{i=1}^{4} E_i + 4.85 \sum_{i=1}^{n} (x \sin^2 \tau_{i,j} + (1-x) \sin^2 \tau_{i,j})$$

$$+ 1.31 \sum_{i=1}^{4-n} (x \sin^2 \sigma_{i,j} + (1-x) \sin^2 \sigma_{i,j}) - 2.11 \times n - 53.95 \qquad (H)$$

where d_i is the bond distance, E_i Pauling's electronegativity, τ_i the torsional angle between the bisect line of the σ(C—H) bonds and the p-orbitals of the adjacent hetero-atoms; σ_i is the corresponding torsional angle involving adjacent σ(C—H) bonds; n is the number of the free orbitals (and thus 4-n the number of adjacent σ-bonds) and finally x is the mole-fraction of one conformation in an eventual binary conformational mixture.

The experimental and calculated coupling constants using equation (H) are in Table 4.

TABLE 4. COMPARISON OF OBSERVED AND CALCULATED VALUES OF $^2J(XCH_2)$ IN CPS FOR A SET OF SELECTED MONO- AND DIHETEROCYCLANES AND ALICYCLIC COMPOUNDS, ACCORDING TO THE BEST FITTING EQUATION (H), INCLUDING DEPENDENCY WITH ELECTRONEGATIVITY BOND DISTANCE, p–σ AND σ–σ TORSIONAL SPATIAL ORIENTATION.
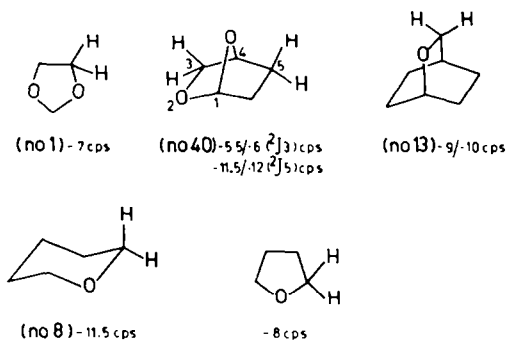
Comp no[a]	1	2	5	7	15	21	25	
$^2J_{ob}$	0/+1	−2·8	−6·2	−11	−11·1	−13·0	−13·5	
$^2J_{calc}$	−0·1[b]	−2·5	−7·4	−10·2	−11·4	−13·3	−13·6	
Comp no	29	31	32	35	36	40	40	1
$^2J_{ob}$	−14·2	−12·3	−11·5	−5·5	−4·7	−5·5/6	−11·5	−7·0[c]
$^2J_{calc}$	−13·9	−12·6	−11·4	−5·0	−3·7	−6·1	−11·8	−6·4

[a] Numbering refers to structures as shown in Fig. 1.

[b] This value becomes −1·0 cps (see also Fig. 4) when one accepts mean ring torsional angles in the COCH₂OC moiety of about 20°, as presumably is the case.[28, 29]

[c] According ref.[31] for $^2J(4)$ of no 1.

CHART II

(no 1) - 7 cps   (no 40) -5·5/·6 (²J₃)cps   (no 13) - 9/ ·10 cps
                   -11·5/·12 (²J₅) cps

(no 8) - 11·5 cps   - 8 cps

Other possible functions

Instead of equation (D) we have tried to do better by taking other possible dependencies into consideration, such as:

$$^2J = -13·0 + \sum_{i=1}^{4} e^{0·68d}\, i + 2·51 \sum_{i=1}^{4} E_i + 4·77 \sum_{i=1}^{4} \sin^2 \tau_i - 4 \times 11·77 \qquad (E)$$

$$^2J = -13·0 + 6·41 \sum_{i=1}^{4} \sqrt{d_i} + 2·69 \sum_{i=1}^{4} E_i + 4·77 \sum_{i=1}^{4} \sin^2 \tau_i - 4 \times 17·42 \qquad (F)$$

$$^2J = -13·0 + 3·69 \sum_{i=1}^{4} d_i \times E_i + 4·76 \sum_{i=1}^{4} \sin^2 \tau_i - 4 \times 18·86 \qquad (G)$$

These expressions were computed each time by iterative procedure in order to define the most suitable coefficients. The relations (E) and (F) give exactly the same results and precision as for (D) while equation (G) is definitely worse. All these programs gave rapid convergency during the iteration on a PDP-8/1 (8-K) computer.
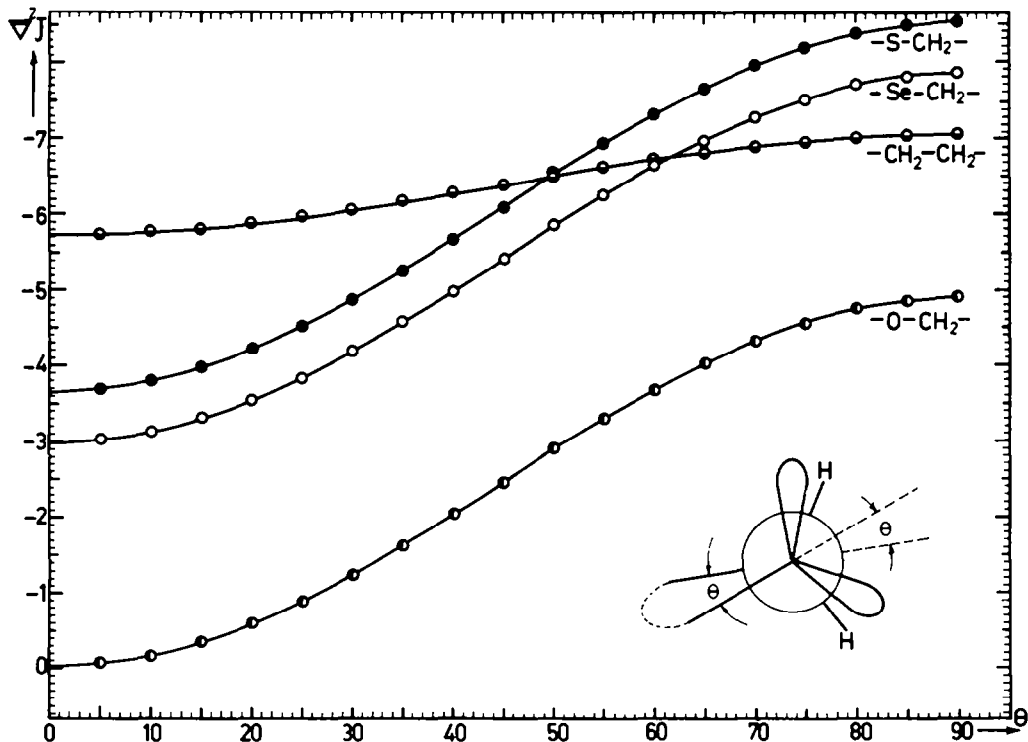
FIG 4. Contribution ∇J to the geminal coupling constant for each neighbour in cyclic compounds (other than small rings) as a function of ring torsional angle (angle between bisecting lines of p and σ orbitals). Calculations are based upon equation (H) and give the contributions to ^2J for X = O, S, Se and C.

Scope and limitations

In Fig. 4 we have pictured the contribution on ^2J of a —CH_2X— moiety, after correction for Pauling's electronegativity and bond distance, as a function of the ring-torsional angle. This angle corresponds with the torsional angle between the two lines, bisecting respectively the (C—H) bonds of the —CH_2— and the two p-orbitals of X. For each kind of X-atom we have a different curve, displaced from each other reflecting changes of E_i and d_i.* Only those for X = O, S, Se and CH_2 are shown, as calculated according to equation (H).

Thus the value for a chair 1,3-dioxane is obtained by taking twice the value found in Fig. 4 at $\theta = 63°$[23] → $-2 \times 3.75 = -7.50$. That for the (ideal) tetrahydropyrane (no. 8) is $-3.65-6.7 = -10.35$ exp. -11 to -11.5 cps. For oxacyclooctane (no. 13) we expect ($\theta = 0$ and $60°$) $-0.1-6.7 = -6.8$, while the experimental value is $9-10$ cps. However in this case we have, strictly spoken, not a CH_2, but a CHX group next to the —O—CH_2— moiety. Moreover the prediction is false due to the fact that both a certain twisting of the oxaethane-bridge[24] and a slight change in hybridization may

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* For X = CH_2 we have a σ-σ parallelity effect instead of a p-σ one. As a result of this we have a different slope of the torsion curve.

occur. Also for the (rigid) dioxabcycloheptane (no. 39) one expects due to the same reasons, a deviation of the experimental value (-5.5 to -6 cps[25]) from the calculated one (-6.12). Also the value of cyclohexane ($\beta = 56°$[32]) is predicted with satisfying accuracy, i.e. -13.2 cps (exp. -13.0 cps).

Let us now discuss further some OCH_2O moieties.

A model for 1,3-dioxane has been synthesized[7] for which the conformation has been accepted to be between that of the chair form and the half-chair (or cyclohexene-like) form as depicted in Chart I (37).

For the half chair form a value is predicted (Fig. 4) of -0.4 cps ($\theta = 0°$ and $15°$), while for the chair form it is -7.4 cps. The experimental value of -3.4 cps points either to the fact we have a heterogeneous conformational mixture ($\approx 50:50$), or to the fact the actual compound takes a conformation which is halfway between both forms, e.g. with ring torsional angles along C_2-O_3 and O_3-C_4 of about $25°$ and $40°$ respectively.

The next molecule we wish to discuss is the cyclohexene-like conformation with alternating axis through C_4-C_5 and C_2-C_1 (Chart I, 38).

For benzenodioxene derivatives a value of ≈ -5.65 was found,*[7] where the predicted value ($\theta = 45$ and $60°$) is ≈ -6.1 cps. In general the calculated values for OCH_2O seem to be somewhat high (see Table 4, 1 and 5); consequently the experiment shows a too negative value. This can be rationalized by a diminution of the electron density in the p-lobes of the oxygen which is in mesomeric interaction with the benzene nucleus. Also the 5-phenyl derivative (Chart I, 38; $L = \phi$) shows a still somewhat more negative value (-6.05 cps)[7] for analogous reasons, and this can be compared with the situation found in acyclic acetals, where methylal has $^2J = -6.0$ cps, but 1-phenyl-2,4-dioxa-pentane has $^2J = -6.6$ cps.[4]

Finally we take an acyclic case for discussion. Methylal has about the same value as the chair 1,3-dioxane (-6.0 and -6.2 cps resp.). That indicates an identical torsional p-σ relation. For methylal we can draw several conformations, e.g. the all-*trans* form (Chart III, 4A), the *trans-skew* (4B), or the two *skew* forms (4C and 4D), (or alternative forms of resp. type IV, III, I and II in the Dunitz–Prelog nomenclature).[26] The predicted values are resp. 0 (IV), -3.55 (III) and -5.90 (I and II) cps.
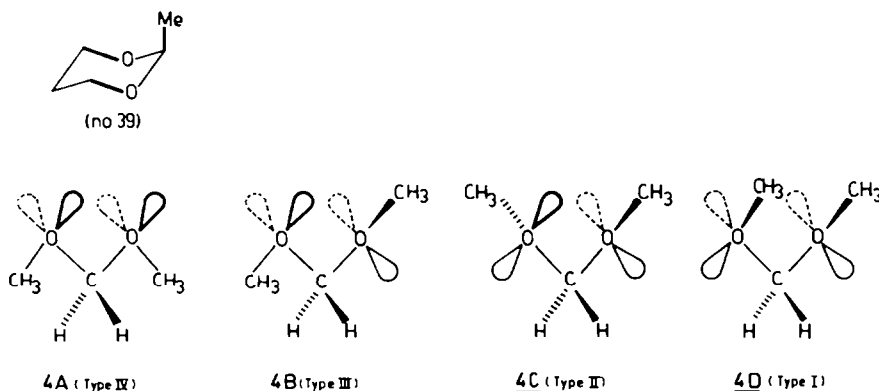

(no 39)

4A (Type Ⅳ)   4B(Type Ⅲ)   4C (Type Ⅱ)   4D (Type I)

CHART III

* This was found to be solvent dependent, and the actual value is that found in CCl_4.

We can exclude the presence of substantial amounts of conformations (4C and 4D) for steric reasons and seemingly the actual conformation for methylal is almost exclusively of type IV. Despite the fact the all-trans form might be favoured with an amount of 2 × 2 Kcal/mole* over the double skew conformation, the latter seems the preferred one.†

We hope to report in the near future on such implications and apparent anomalies. It is reasonable that for such cases, contributions such as valence angle deformation (hybridization of the methyl carbon atom) or changes in electron densities in the p-lobes are at the basis of those exceptions and that with further refinement a more suitable equation, analogous to that which has been derived in the actual paper may be of great importance in the discussion of such effects and conformational implications.

Thus it is obvious that the relation (H) cannot be applied in predicting geminal coupling values in small ring compounds (for which often even positive values are found), mainly because of the disturbed hybridization of the ring-atoms.

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* An exact value cannot be given, but we can compare a skew C—O—C conformation roughly with half the value of $\Delta G°(Me-2)$ in 1,3-dioxane (no. 39), for which 4 Kcal/mole has been proposed.[30]

† Here indeed mutual dipole interaction (as occuring in 4C is minimized. Thus we may accept that $^2J(OCH_2O)$ in methylal will be affected by the polar character of the solvent and of conformational rotameric implications.

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