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# GEMINAL COUPLING CONSTANTS IN METHYLENE GROUPS

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**Abstract**—The effect of electronegativity of α substituents on geminal coupling constants is discussed with particular reference to a recent paper by Anteunis, Swaelens and Gelan.[1]

IN A RECENT PAPER[1] Anteunis, Swaelens and Gelan have severely criticised the linearity of a plot of $J_{gem}$ values in X—CH$_2$—Y methylene groups (X and Y = heteroatoms) against the sum of the Pauling electronegativities of X and Y. That a linear relationship should not exist between these quantities is not surprising since, as Sternhell *et al.*[2] have pointed out, there are no theoretical treatments which suggest that one should exist. However, the Belgian authors imply that we proposed such a relationship and, particularly in a footnote in their paper on page 1918, claim the credit for the uncovering of the lone pair—CH dihedral angle influence on $J_{gem}$ and suggest that we have only recently come to a realisation of the importance of this effect. Since both implications are incorrect we should like to review the situation briefly in order to put matters in their correct perspective.

A molecular orbital treatment[3] of $J_{gem}$ in X—CH$_2$ groups showed that both inductive removal of electrons (from the symmetric bonding orbital of the CH$_2$ group) and back donation of lone pair electrons on X into the antisymmetric bonding orbital produce a positive contribution to $J_{gem}$, and an extensive survey of geminal coupling constants[4] clearly showed the importance of these two effects which were analysed and exemplified at length, as two of four important variables. Thus at this stage (1966) it was already clear that a simple relationship between $J_{gem}$ and electronegativity of an α-substituent could not exist. However in some of our early attempts to provide correlations between $J_{gem}$ and molecular structure we published[5] some plots of $J_{gem}$ in five membered rings and in six membered rings against electronegativities of X and Y. Aware of the lone pair orbital effect on $J_{gem}$ (discussed in the same paper[5] but not acknowledged[1]) we plotted only those values of $J_{gem}$ for compounds which we considered to be in a known conformation. Anteunis *et al.*[1] have reproduced one of our plots and have added other points for conformationally non-homogeneous molecules and for one system at least which is in a non-chair conformation.

This naturally results in an extremely poor correlation between $J_{gem}$ and electronegativity. We are then (twice in the same paper[1]) quoted as excluding five membered ring compounds from the "relationship" although actually we gave[5] a second plot of $J_{gem}$ against electronegativity in five membered ring 1,3- heterosystems. No attempt was made[5] to correlate $J_{gem}$ simultaneously in both six- and five-membered rings with electronegativity since the $J_{gem}$ in the latter compounds are substantially more positive than in the former because of eclipsing of lone pair orbitals with the $CH_2$ bonds. This effect was discussed in detail in the same paper,[5] and to imply that we were later than Anteunis[6] in acknowledging its importance is not borne out by an examination of the published work.

In our original review[4] attention was drawn to the effect of lone pair orbitals on the $J_{gem}$ of a methylene group adjacent to oxygen[13] or nitrogen and the expectation of a continuous variation of $J_{gem}$ with lone pair-CH dihedral angle was expressed. Pople and Bothner-By's MO treatment of geminal coupling constants[3] gave good reason for expecting a lone pair-dihedral angle correlation and this was discussed again in a review on coupling constants.[7] Preceding all these papers was the publication of the results of VB studies[8] on $J_{gem}$ in $CH_2$ C = 0 fragments in which the derived dihedral angular relationship (if not the detailed shape of the curve[4]) has since been amply confirmed by measurements on a range of organic compounds.

In 1966 Anteunis[6] proposed that an increment of 1·8 Hz be added to $J_{gem}$ each time an $\alpha$ oxygen atom or nitrogen atom has one of its lone pair orbitals parallel with the adjacent CH bond. No distinction was made between the effect of eclipsing and anticoplanar lone pairs and no attention was drawn to possible effects dependent on dihedral angle.

The first application of the lone pair-CH—dihedral angle—$J_{gem}$ correlation to a problem in heterocyclic conformational analysis was made in 1966[9] and in a series of subsequent papers[10, 11] this correlation was exploited leading in 1970[12] to the establishment of a curve showing a continuous variation in $J_{gem}$ with $\phi$. Thus in spite of the statement[1] to the contrary there can be no doubt that we have always clearly recognised the lone pair effect.

In Fig. 1 we have again plotted $J_{gem}$ against electronegativity in a series of systems

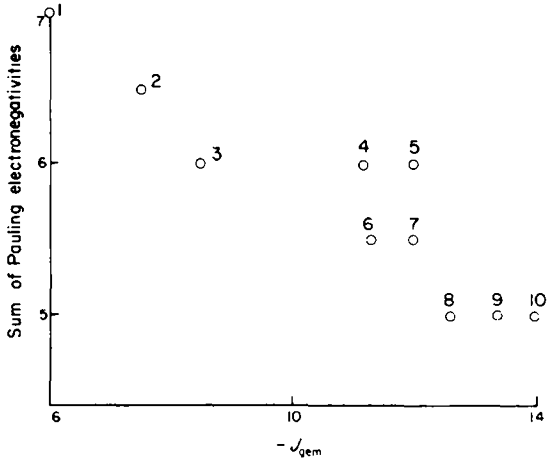


Fig. 1 Plot of sum of Pauling electronegativities of X and Y against $J_{gem}$ in X—$CH_2$ Y methylene groups contained in saturated six-membered ring systems.

1. O—$CH_2$—O in 1,3-dioxams.[13] 2. O—$CH_2$—N in 3,5,5-trimethyltetrahydro-1,3-oxazine[14] and in *trans anti cis* perhydrobenzo *e* pyrido[1,2-*c*][1,3]oxazine.[11b] 3. N—$CH_2$—N in 1,3,5,5-tetramethylhexahydropyrimidine[15] and in *trans syn trans* perhydrodipyrido[1,2-*c*; 2′1′-*f*]pyrimidine.[11c] 4. O—$CH_2$—S in 1,3-oxathians.[16] 5. O—$CH_2$—C in tetrahydropyran.[17] 6. N—$CH_2$—C in quinolizidine.[18] 7. N—$CH_2$—S in 3-thia-1-azabicyclo[4.4.0]-decane.[11a] 8. C—$CH_2$—C in cyclohexane.[19] 9. S—$CH_2$—C in thians.[20] 10. S—$CH_2$—S in 1,3-dithians.[16]

which are conformationally fairly well defined including only those systems with the lone pair—CH parallel geometry: the rough correlation is apparent. If instead of electronegativity a more complex expression containing a sufficient number of variables were employed naturally a linearity of plot could be achieved. In the expression recently developed[1] $J_{gem}$ is related to C—X bond distance, electronegativity of substituents, torsional angles of the methylene with adjacent lone pair and CH orbitals and the number of adjacent lone pairs. In this expression the effect of angular distortion on $J_{gem}$ was intentionally neglected: it has, however, been shown to be an important factor[4] and allowance for it does improve the correlation in Fig. 1.

In the case of the sulphur-containing compounds there must be a negative contribution to $J_{gem}$ from the enlarged S—C—C or S—C—X bond angle. Thus in cyclohexane the endocyclic angle ($\alpha$) is 111·5°,[21] whereas in 2-phenyl-1,3-dithian the endocyclic S—C—S angle is 115·2° and the C—C—S angle 114·9°.[22] Thus there is a $\Delta\alpha$ between cyclohexane and the compounds containing sulphur of 3·7 to 3·4°. Reference to our correlation[4] between $J_{gem}$ and $\alpha$ shows that in this region of the curve a $\Delta J_{gem}$ of *ca.* 2 Hz is expected. Thus points 4,7,9, and 10 can be shifted to larger $J_{gem}$ values. In trioxan ($J_{gem} = -6$ Hz) the endocyclic O—C—O angle is 107·8°[23] and there might then be, relative to cyclohexane, a positive contribution to $J_{gem}$ of *ca.* 1 Hz. Thus we can shift point 1 to a more negative $J_{gem}$ value. The argument probably applies also to the hexahydropyrimidines and tetrahydrooxazines 2 and 3 but no data are available on the angles in these systems.

In the compounds containing oxygen and nitrogen there is a positive contribution to $J_{gem}$ from the parallel heteroatom lone pairs. Since the lone pairs on nitrogen are less firmly held than on oxygen we might expect more efficient transfer of the nitrogen lone pairs into the antisymmetric $CH_2$ orbital than in the case of the oxygen lone pairs, and so the nitrogen heterocycles are made more positive by this effect than

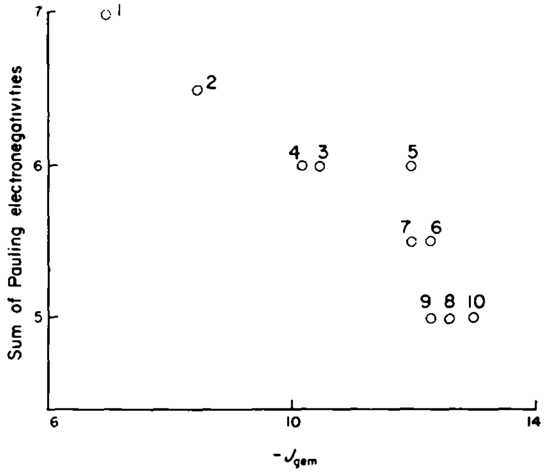
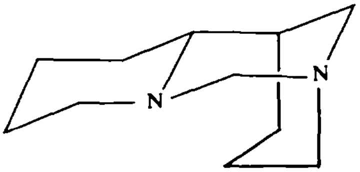


FIG. 2. Plot of sum of Pauling electronegativities of X and Y against $J_{gem}$ in X—$CH_2$—Y methylene groups contained in saturated six-membered ring systems adjusted for endocyclic angle effect and nitrogen lone pair effect.

the oxygen heterocycles. We can then adjust points 2,3,6 and 7 with twice as much adjustment (2 nitrogen lone pairs) to 3 than to 2 (one nitrogen lone pair). The results of these adjustments are shown in Fig. 2. To avoid any future misunderstanding we must leave the reader to draw his own line through the points.



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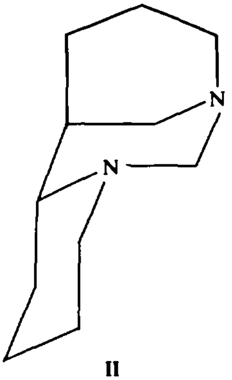

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In conclusion, two warnings on prediction of $J_{gem}$ in 1,3-heterosystems must be made. Reference to the two triads of compounds 8,5,1 and 8,6,3 (Fig. 1) suggests that the electronegativity effect on $J_{gem}$ cannot be additive and that the electronegativity effect of two heteroatoms is more than twice that of one, as already pointed out.[4] The mutual interaction of two heteroatoms thus can not be ignored. Secondly, reference to the pair of compounds I and II in which p-σ and electronegativity effects might be predicted to be the same show $J_{gem}$ values of $-11{\cdot}3$ and $-10{\cdot}5$ Hz respectively.[12] Thus at this stage the application of $J_{gem}$ to stereochemical problems should best proceed by comparison of values from related systems. Any attempt to quantify the relationships universally is in danger of leading to a similar situation to that occurring after the Karplus relationship[24] was introduced, in spite of warnings.[25]

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