The Effect of Adjacent Heteroatoms (groups) on the Magnitude of J_{gem}

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Summary Empirical relationships have been derived for the variation of J_{gem} with respect to the orientation of the lone pairs on the adjacent oxygen and sulphur atoms; a similar relationship has been obtained for a sulphone group but a different one for a sulphoxide group.

IT was predicted[1] on the basis of MO theory that J_{gem} should become more positive when a heteroatom attached to the methylene group can withdraw inductively electrons from the ψ_1 orbital of the methylene and back donate them from the lone pair(s) into the ψ_2 orbital. The latter effect should be dependent on the dihedral angle, θ, between the lone pair(s) and one of the hydrogens; it should be at maximum when $\theta = 0°$. ($\theta = 0°$ when the protons of the methylene group are eclipsed with the lone pairs and/or the S–O bonds).

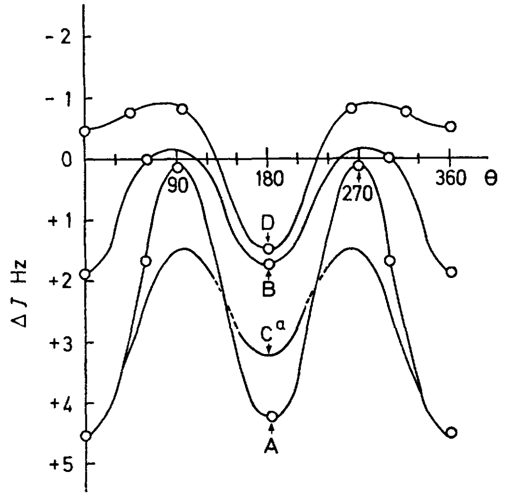
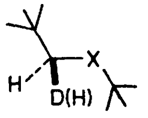


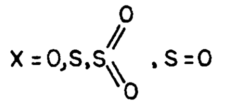
Figure 1

[a] The theoretical curve C[2] could have been "anchored" on our experimental curve A at $\theta = 90°$ (270°) or 180°. We chose $\theta = 0°$ (360°) because this point represents ΔJ derived from the largest number of compounds.

The experimental verification of this prediction for oxygen (Figure 1, Curve A) and for sulphur (Figure 1, Curve B) satisfactorily reproduces the theoretical conclusions. Indeed a similar shaped curve to oxygen has recently been theoretically derived for methanol[2] (Figure 1, Curve C).

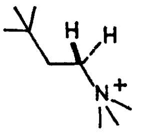
Most of the points forming the curves have been collected from the literature and the data will be published in a full publication. The compounds for the 180° orientation were synthesised for this study; they are all of the type:





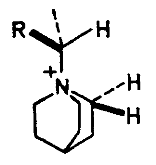
$X = O, S, SO_2, S{=}O$

The curves A and B show that ΔJ_{gem} is virtually zero at certain values of θ (90° and 270°). This indicates that the dominant factor that controls the magnitude of J_{gem} is the donation of electrons to the antisymmetric bonding orbital ψ_2, and that the inductive withdrawal from ψ_1 is negligible. This conclusion is supported by values of J_{gem} adjacent to a quaternary nitrogen atom in compounds (**1**)[3] and (**2**)[4]. The more positive ΔJ_{gem} produced by adjacent oxygen than by adjacent sulphur is possibly due to the smaller separation between the energy level of a C–H bond and the energy level of an oxygen lone pair in comparison with that of a sulphur lone pair; this enables greater back donation into ψ_2 to take place from oxygen.



(1)

-12·5 ± 0·1 Hz



(2)

R = Ph 12·5 Hz

= CO_2Et 12·5 Hz

The sulphone curve (Figure 1, Curve D) is qualitatively similar to the oxygen and sulphur curves, but ΔJ_{gem} in certain orientations is negative, suggesting a withdrawal of electrons from the antisymmetric bonding orbital ψ_2.† There may be some compensating back-donation from the oxygen atoms, especially at $\theta = 180°$.

Probably the most interesting relationship in the change of J_{gem} is due to the adjacent sulphoxide group (Figure 2, Curve E). The asymmetry of the group can be seen from the curve, which has no symmetry about 180°, whereas curves A, B, and D in Figure 1 are all symmetrical about 180°. The values of ΔJ_{gem} indicate both electron donation to ψ_2 in certain orientations by the single lone pair, and electron withdrawal from the same orbital by the sulphur-oxygen bond.† In fact, a curve similar in shape (Figure 2, Curve F) can be constructed from two curves; one that resembles the curve obtained for a bromine atom attached to an adjacent carbon atom[5] (negative ΔJ_{gem}, Figure 2, Curve G) and the other a reflection of this same curve displaced by 120° (positive ΔJ_{gem}, Figure 2, Curve H). A similarly shaped curve to the latter has recently been derived for the angular contribution of the lone pair on nitrogen.[6]

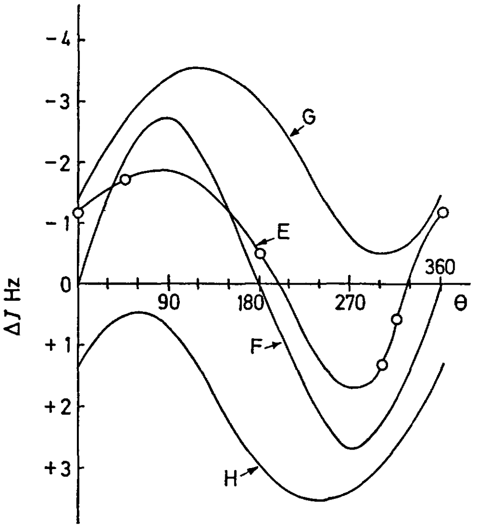


Figure 2

The direction of rotation for the unsymmetrical sulphoxide group is such that the lone pair bisects the adjacent methylene protons when $\theta = 60°$.

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† This might possibly be accomplished by using the partially vacant orthogonal π-orbital on sulphur or the σ^*-orbital of the sulphur–oxygen bond.

The J_{gem} of various cyclic systems incorporating the above groups X can be calculated by adding the ΔJ_{gem} to the appropriate J_{gem} of the carbocyclic system, *e.g.* cyclobutane $J_{gem} = - 11{\cdot}0$ Hz, cyclopentane and cyclohexane $J_{gem} = - 13{\cdot}0$ Hz.

The measurements were performed in $CDCl_3$ on a Varian HA100 instrument equipped with an external frequency sweep oscillator.

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