Relationship between the Magnitude of a Geminal Coupling Constant and a Dihedral Angle of a β -Substituent

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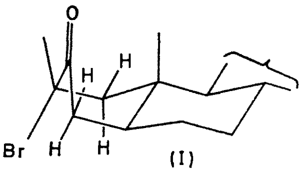
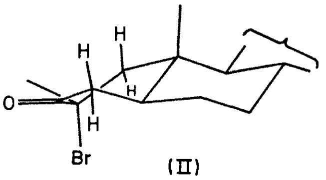
Summary An experimental curve was obtained for the above relationship with bromine as a substituent and utilised for a solution of a conformational problem

IT was predicted that J_{gem} should become more positive when an electronegative substituent on the β-carbon is in the plane that bisects symmetrically the methylene group and more negative when the substituent is perpendicular to the same plane [1,2]



(I)



(II)

Our compilation of geminal coupling constants[3] and current work on the halogenation of ketones[4] provided J_{gem} values that have enabled us to construct an empirical curve for a β-bromine (Figure) Although the magnitude of ΔJ between the two axial conformations (60—180°) is at present uncertain,† it appears that the relationship will have a periodicity of 360° Our work also shows that other β-substituents such as F, Cl, OH, OAc, OMe CN, and an oxygen of a sulphoxide group give curves of similar shape but the magnitudes of ΔJ_{ecl}, ΔJ_{ax}, and ΔJ_{eq} vary Furthermore, the increments for various substituents are additive Thus the application of the ΔJ_{ecl} values to the

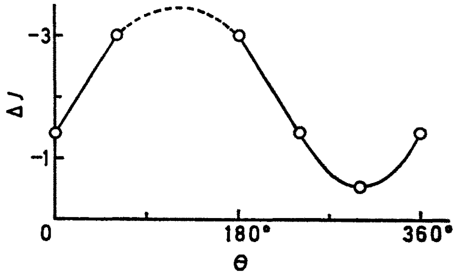


FIGURE *Dihedral angles are defined as eclipsed* 0°, 240°, 360°, *axial* 60°, 180°, *equatorial* 300° *The points were derived from* J_{gem} *of compounds quoted in the following references Standard compounds with unperturbed* J_{gem} *are in italics*
Eclipsed W E Rosen, L Dorfman and M P Linfield, *J Org Chem* , 1964, **29**, 1723, P Laszlo and P Schleyer *J Amer Chem Soc* 1963, **85** 2709, endo 2-*hydroxymethylbicyclo*[2,2 1]*hept*-5-*ene* $J_{3\ \text{gem}}$ −11 2, J M Mellor, unpublished work, F Piozzi, A Quilico T Ajello, V Spiro, and A Melera, *Tetrahedron Letters*, 1965 1829, L E Erickson, *J Amer Chem Soc* 1965, **87** 1867, F W Lichtenthaler and A El Scherbiney, *Chem Ber* , 1963, **101** 1799 *Axial* 2 2 4,4 *tetradeuteriocholestanone* $J_{1\ \text{gem}}$ −12 5, 2β bromocholestanone $J_{1\ \text{gem}}$— 15 7, 2β—bromo-2α deuteriocholestanone $J_{1\ \text{gem}}$ −15 6, 2β bromo 2α-methylcholestanone $J_{1\ \text{gem}}$ −16 0, 2,2 dibromocholestanone $J_{1\ \text{gem}}$ −15 5, ref 4, J -C Jacquesy and J Levisalles *Bull Soc chim France*, 1962 1866 *Equatorial* 2α-bromocholestanone $J_{1\ \text{gem}}$ −13 0, 2α-bromo 2β-deuteriocholestanone $J_{1\ \text{gem}}$ −13 0, 2α bromo-2,4 4-trideuteriocholestanone $J_{1\ \text{gem}}$ −13 0 ref 4

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† We are currently engaged in synthesis of compounds that will yield this information.

geminal coupling constants of substituted cyclobutanes[3] gives the J_{gem} of cyclobutane $-11{\cdot}0 \pm 0{\cdot}5$ Hz, which is in excellent agreement with the recently determined value of $-10{\cdot}9$ Hz.[5]

The utility of this relationship to conformational analysis can be seen from the following example. Djerassi *et al.*[6] assigned the boat conformation (I) to the kinetic product of bromination of 2α-methylcholestan-3-one on the basis of o.r.d., u.v., and i.r. results. Thus, one would expect $J_{1\ \text{gem}}$ $-14{\cdot}0$ and $J_{4\ \text{gem}}$ $-13{\cdot}0$ to $-14{\cdot}0$ Hz[1,3,7] for (I). However, the experimental values are $J_{1\ \text{gem}}$ $-15{\cdot}7$ and $J_{4\ \text{gem}}$ $-16{\cdot}6$ Hz. These values are compatible only with the other possible boat conformation (II) of ring A.[3,7]

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[1] J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, 1965, **42**, 1339.
[2] A. A. Bothner-By, *Adv. Magnetic Resonance*, 1965, **1**, 195.
[3] R. C. Cookson, T. A. Crabb, J. J. Frankel, and J. Hudec, *Tetrahedron*, *Suppl.* 7, 1966, 355.
[4] J. Hudec, unpublished work.
[5] K. Wiberg and D. E. Barth, *J. Amer. Chem. Soc.*, 1969, **91**, 5124.
[6] C. Djerassi, N. Finch, R. C. Cookson, and C. W. Bird, *J. Amer. Chem. Soc.*, 1960, **82**, 5488.
[7] M. Barfield and D. M. Grant, *J. Amer. Chem. Soc.*, 1963, **85**, 1899.