

EXTENDED HÜCKEL THEORY MO CALCULATIONS OF PROTON-PROTON
COUPLING CONSTANTS. THE SUBSTITUENT EFFECT IN FLUOROETHANE.

K.G.R. Pachler
Chemical Physics Group, Council for Scientific
and Industrial Research, Pretoria, South Africa.

(Received in UK 1 April 1970; accepted for publication 9 April 1970)

INTRODUCTION

It is well established experimentally, that the magnitude of vicinal proton-proton coupling constants in HC-CH fragments with sp^3 hybridised carbon atoms depends mainly on two factors: (a) the dihedral angle between the coupling protons and (b) the electronegativity and relative orientation of substituents. The angle dependence has been calculated repeatedly by VB and MO methods and is described by the well-known Karplus equation¹. However, no detailed theoretical assessment of the substituent effect has as yet been reported. This communication presents the results of EHT MO calculations of the vicinal proton-proton coupling constants in fluoroethane as a function of the dihedral angle, demonstrating the effect of an electronegative substituent.

RESULTS

The coupling constants were calculated by the method of Fahey *et al.*², which is based on the recently developed theory of Pople and Santry³. One-electron wave functions and energies were obtained from EHT MO calculations using all valence-shell orbitals and including overlaps⁴. The vicinal proton-proton coupling constants obtained for fluoroethane as a function of the dihedral angle ϕ_{HH} are shown in Figure 1. The angle θ_{XH} between the substituent and the coupling proton on the next carbon atom is defined such that $\theta_{XH} = \phi_{HH} - 120^\circ$ (*cf.* Figure 1).

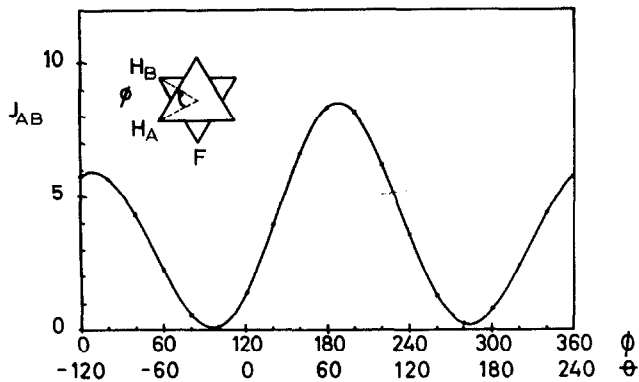


Figure 1 : The vicinal coupling constant J_{AB} of fluoroethane versus the dihedral angle ϕ_{HH} .

The angle dependence of the coupling constant is obviously quite similar to the relationship obtained by Karplus for ethane. However, a small phase shift is observed and the curve is no longer symmetrical about $\phi_{HH} = 0^\circ$, *i.e.* coupling constants for the same dihedral angle ϕ_{HH} may be different, depending on the corresponding substituent angle θ_{XH} . The calculated values are represented by an equation of the type

$$(1) \quad J_{AB} = A + B \cos \phi + C \cos 2 \phi + D \sin \phi + E \sin 2 \phi$$

with $A = 3.68$, $B = -1.21$, $C = 3.35$, $D = -0.20$, $E = 1.12$ and an RMS error of 0.1 Hz.

The effect of the substituent is best demonstrated by the difference $J_{\text{ethane}} - J_{\text{fluoroethane}}$ shown in Figure 2. It is interesting to note that an increase of the coupling constant is predicted for certain ranges of ϕ_{HH} .

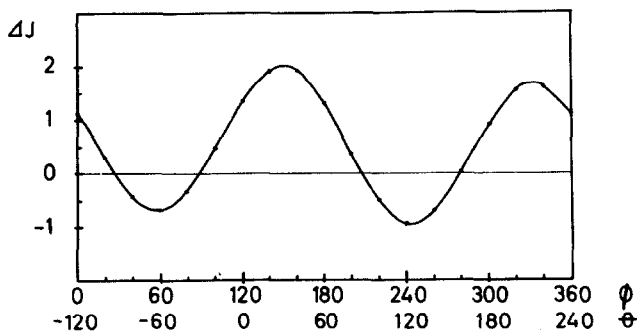


Figure 2 : The difference of the vicinal coupling constants in ethane and fluoroethane ΔJ versus the dihedral angle ϕ_{HH} .

Further calculations at present in progress indicate that the observations made on fluoroethane are common to monosubstituted ethanes, and that the constants in equation (1) are simple functions of the electronegativity of the substituent. One may therefore assume that Figure 2 represents, qualitatively, the general effect of electronegative substituents.

DISCUSSION

It is known that the average vicinal coupling constant in substituted ethanes and related saturated organic compounds decreases approximately linearly with the sum of the electronegativity of all substituents attached to a HC-CH fragment,^{5,6} that the electronegativity effect is strongly dependent on the relative position of the substituent and the coupling protons,^{7,8} and that an increase with electronegativity is observed for certain conformations^{9,10}. All these features are reproduced by the present calculations. Restricting the discussion to fixed conformations, it is predicted for staggered conformers that the gauche coupling will increase if an electronegative substituent is in a gauche position relative to one of the coupling protons, but will decrease if the substituent is trans. A trans coupling, which can only have gauche substituents, will always decrease. This agrees well with experimental observations on the coupling constants of the individual rotational isomers of 1,2-disubstituted ethanes¹⁰. The gauche couplings of the trans isomers, having two electronegative substituents in gauche position, increase; all other couplings decrease as predicted.

In eclipsed conformations, as encountered in rigid bicyclic ring systems, a decrease of the *cis* (J_0) and *trans* (J_{120}) couplings is expected from these calculations, if the substituent angles θ_{XH} are 120° and 0° , respectively. The coupling constants in norbornene derivatives and in particular in hexachlorobicyclo [2.2.1] heptenes¹¹, provide clear evidence for this effect.

Finally, an increase of the coupling constant with the substituent electronegativity is predicted if both angles ϕ_{HH} and θ_{XH} are 120° . It is difficult to find unambiguous experimental support in this case, since model compounds are required to have hetero-atoms in a rigid ring system. Conformational changes as well as the effects of lone pair electrons obscure the electronegativity effect. However, extrapolation of the couplings in hexachlorobicycloheptene derivatives leads to the following values for an eclipsed C-CH₂-CH₂-C system: $J_0 = 9.4$ Hz, $J_{120} = 4.7$ Hz. Comparison with the corresponding coupling constants in the N-CH₂-CH₂-N fragment of 1,4-diazabicyclo [2.2.2] octane¹² ($J_0 = 9.27$ Hz, $J_{120} = 5.93$ Hz) lends some support to the

prediction that J_{120} increases with substituent electronegativity.

REFERENCES

- 1) M. Karplus, *J. Chem. Phys.* 30, 11 (1959).
- 2) R.C. Fahey, G.C. Graham, R.L. Piccioni, *J. Am. Chem. Soc.* 88, 193 (1966).
- 3) J.A. Pople, D.P. Santry, *Mol. Phys.* 8, 1 (1964).
- 4) R. Hoffmann, *J. Chem. Phys.* 39, 1397 (1963).
- 5) R.E. Glick, A.A. Bothner-By, *J. Chem. Phys.* 25, 362 (1956).
- 6) R.J. Abraham, K.G.R. Pachler, *Mol. Phys.* 7, 165 (1963).
- 7) D.H. Williams, N.S. Bhacca, *J. Am. Chem. Soc.* 86, 2742 (1964).
- 8) H. Booth, *Tetrahedron Letters* 411 (1965).
- 9) M. Witanowski, J.D. Roberts, *J. Am. Chem. Soc.* 88, 737 (1966).
- 10) R.J. Abraham, G. Gatti, *J. Chem. Soc. (B)*, 961 (1969).
- 11) K.L. Williamson, *J. Am. Chem. Soc.* 85, 516 (1963).
- 12) D.B. MacDonald, Ph. D. thesis, Liverpool University (1966).