The Dependence of Vicinal Proton-Proton Coupling Constants of Norbornenes on Molecular Structure

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A modification of the Karplus equation, containing four mutually independent structural terms and five adjustable parameters, is put forward. The new structural factor, introduced into this modification is $\sin(\theta_1 + \theta_2)/2$. The new equation reproduces experimental NMR vicinal coupling constants of norbornenes with a standard deviation of about 0.45 Hz.

Key words: Norbornenes; Coupling Constants; Molecular Mechanics; Karplus Equation; NMR.

Introduction

The need for an accurate description of vicinal coupling constants in organic chemistry is evident. ^{1}H NMR has been widely used for the solution of conformations of molecules. The pioneering application of NMR in determining the conformation of molecules in solution was made by Karplus. He introduced the equation [1, 2]

$$J = A\cos\omega + B\cos 2\omega + C\,, \tag{1}$$

where ω represents the dihedral angle between the coupling protons, whereas A, B, and C are adjustable parameters. Unfortunately, the usefulness of ^{1}H NMR in conformational analysis is not always realized because of the lack of an accurate functional relation between J and the torsional angle between protons. For that reason, factors such as H-C-C internal angles, C-C bond lengths and electronegativities of substituents were included into the numerous modifications of the Karplus equation [3–6]. All these modifications have more parameters than the original Karplus equation. The formula of Haasnoot et al. [6] is the most widely used expression for the calculation of coupling constants. However, all these equations including that of Haasnoot, can not reproduce experimental coupling constants of vicinal protons of norbornenes with a satisfactory accuracy.

Osawa's formula [7–10]

$$\begin{aligned} J = {} & A\cos\omega + B\cos 2\omega + C\cos 3\omega \\ & + D\cos^2 2\omega + W(E\cos\omega \textstyle\sum \Delta\chi_i \cos\phi_i \\ & + F\textstyle\sum\Delta\chi_i \cos 2\phi_i + G\textstyle\sum\Delta\chi_i) \\ & + H\,[(\theta_1+\theta_2)/2 - 110] + I\,(r_{\text{C-C}} - 1.5) \\ & + K\textstyle\sum\Delta\chi_j^\beta \cos 2\psi_j + L\,r^{-4} + M\,, \end{aligned} \tag{2}$$

where ϕ is the dihedral angle between the α substituent R_i and one of the coupling protons, $\Delta\chi_i$ Mually's electronegativity [11] of R_i, $\Delta\chi_j^\beta$ that of the j-th β-substituent R′ forming a dihedral angle ψ with a coupling proton, θ_1 and θ_2 are the two H-C-C valence angles involving a coupling proton, $r_{\text{C-C}}$ is the distance of the C-C bond, r the intramolecular nonbonded distance (less than 3.3 Å) involving a coupling proton and oxygen or carbon atom, and A to I, K to M and W are the adjustable parameters. Experimental values of coupling constants of vicinal protons of norbornenes were reproduced by this formula with RMS = 0.572 Hz. For this purpose a set of 32 experimental values was used [7].

Barfield and Smith suggested the formula:

$$\begin{aligned} J = {} & 33.8\,a(\theta_1,\theta_2)\cos^2\phi \\ & + [-1258.4\,b_1(\theta_1,\theta_2)\,650.5\,b_2(\theta_1,\theta_2) \\ & - 905.3\,b_3(\theta_1,\theta_2)]\cos\phi - 0.3\text{ Hz}\,, \end{aligned} \tag{3}$$

where a, b_1, b_2 and b_3 are complicated functions of internal H-C-C angles [12]. For the base of 26 experimental coupling constants of vicinal protons of norbornenes, this equation has RMS = 0.984 Hz [13] which is considerably weaker than that of Osawa.

Up to now, Osawa's formula turned out to be the most suitable equation for reproducing coupling constants of norbornenes. Our aim was to find a simpler expression for J, that would maintain the accuracy of Osawa's formula [7].

Methodology

In our investigations the molecular mechanics program package PCMODEL, version 4.0 [13, 14], was used. This program is based on the MMX force field, derived from Allinger's MM2 force field [15]. A variety of experimentally determined vicinal proton-proton

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coupling constants of norbornenes is available in the literature. In order to minimize the errors of calculations, all rotamers were taken into account. In this manner a set of 72 vicinal proton-proton coupling constants was formed, in which both H-atoms are bound to sp^3 carbon-atoms. In addition to this, we formed a set of 17 such coupling constants, in which at least one hydrogen is bound to an sp^2 C-atom. In the latter set, in 7 molecules both coupling protons are attached to sp^2 C-atoms, whereas in 11 molecules only one coupling proton is bonded to an sp^2 carbon [16].

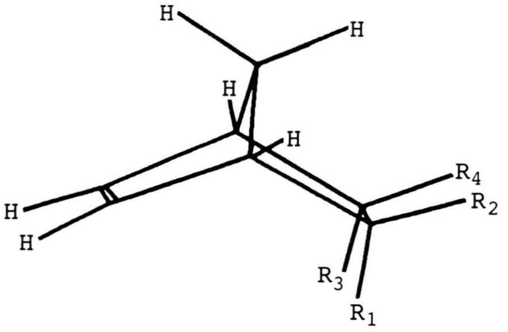

Fig. 1. The structure of norbornenes. R_1, R_2, R_3, and R_4 are the substituents.

Results and Discussion

The structure of the compounds investigated is presented in Figure 1. Here, R_1, R_2, R_3, and R_4 represent H atoms or CN, COOH, OH, Cl, Br, OR, and Ac substituents. The list of experimental data, compounds, results of calculation and literature information is available from the authors on request.

In an earlier investigation [17] the following formula was proposed for the calculation of the coupling constants of compounds other than norbornenes:

$$J = A r + B |\cos \omega| + C \sum \Delta E_i^{\alpha} + D n , \tag{4}$$

where r is the intramolecular nonbonding distance between coupling protons, n the number of substituents attached to the H-C-C-H fragment, and $\sum E_i^{\alpha}$ stands for Mually's sum of electronegativities [11]. It was shown [17] that vicinal coupling constants are dependent on the electronegativities of substituents, but this dependence is not of crucial significance. Therefore the electronegativity term in (4) is now replaced by the expression $\sin(\theta_1 + \theta_2)/2$, where θ_1 and θ_2 are corresponding bond angles between the coupling protons (Figure 2). We also tested several functions of the torsional angle, $|\cos \omega|$, $\cos 2\omega$ and $\cos^2 \omega$. Our calculations showed that the function of the form $|\cos \omega| + \cos^2 \omega$ is most suitable for use. In this way (5) is obtained:

$$J = A |\cos \omega| + B \cos^2 \omega + C r + D n + E \sin \frac{\theta_1 + \theta_2}{2} . \tag{5}$$

The number of substituents, n, is 2, 3 or 4 for the 1,1-di, tri and tetra substituted ethane fragment (Fig. 2), respectively; A, B, C, D and E are adjustable parameters (Table 1). The quality of (5) is conveniently judged by the root mean square criterion RMS (standard deviation). For the set of 72 coupling constants, RMS was found to be 0.4468. By introducing a free term into (5), its quality is not significantly improved. This fact was verified also by the F-test.

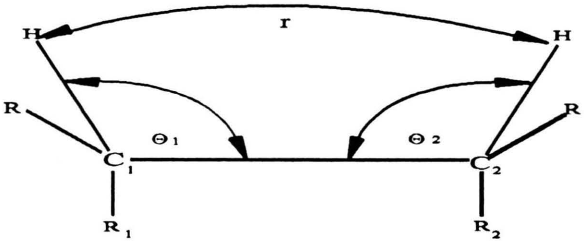

Fig. 2. Schematic representation of the ethane fragment. C_1 and C_2 denote the carbon atoms directed towards the coupled hydrogen atoms H. The internal bond angles H-C_1-C_2 and H-C_2-C_1 are denoted by θ_1 and θ_2, respectively. The intramolecular distance between coupling protons is denoted by r. Rs denote part of ring, whereas R_1 and R_2 are substituents.

Table 1. Optimum set of parameters for (5) fitted to 72 experimental vicinal proton-proton coupling constants of norbornenes.

A	*B*	*C*	*E*
−9.1022	13.0006	0.9207	−58.7998
	1,2 Di	Tri	Tetra
D	−25.8686	−17.6480	−13.2789

Table 2. Relative importance of terms occurring in (5).

Term	$\lvert\cos \omega\rvert$	$\cos^2 \omega$	r	n	$\sin(\theta_1 + \theta_2)/2$
RMS	0.5163	0.6950	0.4639	0.6115	0.5454

In Table 2 the relative importance of various terms in (5) is presented. One can observe that $\cos^2 \omega$ and

$\sin(\theta_1 + \theta_2)/2$ are the most important factors influencing the magnitude of the coupling constants, whereas the distance between the coupling protons is of minor statistical importance.

The investigations mentioned above were performed on protons attached to sp^3 C-atoms. Equation (5) yields surprisingly good results also when applied to protons attached to double bonds and reproduces the coupling constants of vicinal protons of the fragment $R_2C = CH - CHR_2$ with RMS = 0.1794. If a correction factor K is included into (5),

$$J = A\,|\cos\omega| + B\cos^2\omega + C\,r + D\,n + E\sin\frac{\theta_1 + \theta_2}{2} + K\,, \qquad (6)$$

with $K = 0.0933$ to the same molecular fragments the RMS value is even better (RMS = 0.1479). In the case of RCH = RCH fragments, by the use of (6) with $K = 4.2942$ the values of vicinal coupling constants are reproduced with RMS = 0.1938.

Conclusion

Equations (5) and (6) are modifications of the Karplus formula. They are distinguished by a relatively small number of terms with retained satisfactory accuracy for the calculation of vicinal coupling constants of norbornenes and depend only on the structure of the norbornene molecule. They contain the following structural factors: dihedral angle, bond angles and distance between the coupling protons. It is worth noting that (6) can be understood as a universal formula for calculating vicinal coupling constants of norbornenes, because it pertains also to protons of unsaturated parts of the molecule. We hope that it will find applications in the stereochemical considerations of norbornenes.

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