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Dependence on saccharide conformation of the one-bond and three-bond carbon–proton coupling constants*,†

Igor Tvaroška
Institute of Chemistry, Slovak Academy of Sciences, 842 38 Bratislava (Czechoslovakia)

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ABSTRACT

A theoretical study is presented of the dependence on conformation of $^1J_{C,H}$ and $^3J_{C,H}$ values in model compounds related to glycosides. Calculated J values for dimethoxymethane and 2-methoxytetrahydropyran are based on the FPT formulation in the semiempirical INDO method. The configuration at the anomeric carbon affects the $^1J_{C,H}$ value, and the $^1J_{C,H}$ and $^3J_{C,H}$ values vary characteristically with dihedral angle about the carbon–oxygen bond. The agreement of the calculated and experimental values is satisfactory, especially for the $^3J_{C,H}$ values.

INTRODUCTION

An understanding of the biological function of carbohydrates depends largely on the information available about their structure in solution. The conformational properties of simple and complex saccharides have been determined largely by exploiting the n.O.e.'s and J values obtained from n.m.r. spectra.

Interest in the conformational properties of glycosidic linkages, which determine the spatial arrangement of oligo- and poly-saccharide chains, has focused attention on $^3J_{C,H}$ values. However, the difficulties in determining these values experimentally and their small magnitudes have limited their exploitation. On the other hand, the calculation of $J_{C,H}$ values can provide information on the factors that control their magnitudes.

A general rule that, for an equatorial C–H bond, $^1J_{C\text{-}1,H\text{-}1}$ is ~ 10 Hz higher than for an axial C–H bond has been established[1–3]. This effect might be due to different proximities of the hydrogen to the lone pair of electrons on the ring oxygen atom[3] or to small changes in bond angles, which influence the *s*-character of the C–H bond[4]. The difference is influenced markedly by the substituents on non-anomeric carbon atoms and may even become negligible[5].

$^3J_{C,H}$ values have been studied extensively[6], including those which provide a

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measure of the dihedral angles Φ and Ψ about the C–O glycosidic bonds. Consequently, much effort has been invested[7-13] in order to establish the dependence of $^3J_{C,H}$ values on Φ and Ψ in C–O–C–H arrays, and equation *1* has been derived[14] by using conformationally rigid carbohydrate derivatives and 2D-n.m.r. techniques[15].

$$^3J_{C,H} = 5.7\cos^2\varphi - 0.6\cos\varphi + 0. \qquad (1)$$

Information on the magnitude of $^1J_{C,H}$ and $^3J_{C,H}$ values as a function of φ and ψ will be of value for the determination of conformational behavior of carbohydrates. Despite the complexity of the physical situation, useful structural data may be obtainable from $^1J_{C,H}$ and $^3J_{C,H}$ values associated with the anomeric region of carbohydrates in solution. The dependence of these values on Φ and Ψ has been investigated by the finite perturbation theory (FPT) formulation for nuclear spin–spin coupling in the intermediate neglect of differential overlap (INDO) approximation of semiempirical molecular orbital (MO) theory[16] as applied to the model systems, dimethoxymethane (**1**) and 2-methoxytetrahydropyran (**2**) with an axial (**2a**) and equatorial methoxy group (**2e**), and the calculated results compared with the available experimental data.

RESULTS AND DISCUSSION

Molecular orbital description of the conformational dependence of $^1J_{C,H}$. — *(a) Dimethoxymethane* (**1**). Calculated INDO–FPT values of $^1J_{C,H}$ for the methylene group of **1** were based on the experimental gas-phase geometry[17]. The calculated results are

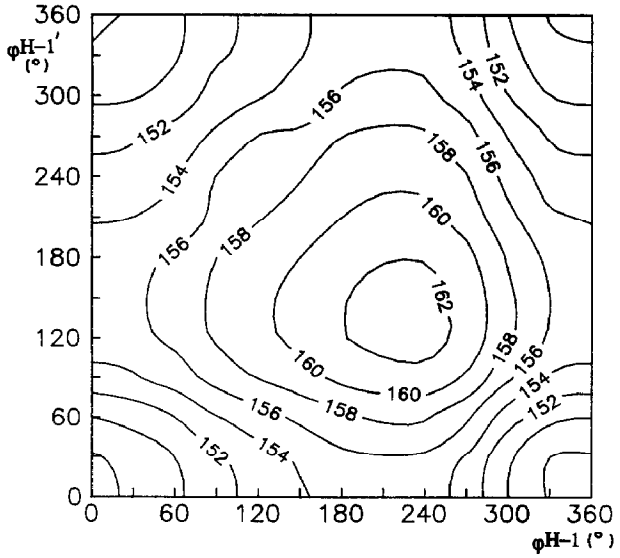

Fig. 1. Contours of the calculated INDO–FPT results for the $^1J_{C,H}$ values (Hz) of the methylene group of dimethoxymethane (**1**) as a function of $\varphi^{H\text{-}1}$ and $\varphi^{H\text{-}1'}$.

plotted as a function of $\varphi^{H\text{-}1}$ and $\varphi^{H\text{-}1'}$ around the central C–O bonds in Fig. 1; $\varphi^{H\text{-}1}$ and $\varphi^{H\text{-}1'}$ (H–C–O–O) are related to the usual dihedral angles φ_1 (O–C–O–C) by the relationship $\varphi^{H\text{-}1} = \varphi_1 + 120°$ and $\varphi^{H\text{-}1'} = \varphi_{1'} - 120°$. The absolute minimum of 147.6 Hz occurs at $(\varphi^{H\text{-}1}, \varphi^{H\text{-}1'}) = (0°,0°)$, *i.e.*, for the conformation in which each O–CH_3 bond is eclipsed with a C–H bond. Rotation about the CH_2-O bond towards the other C–H bond increases the $^1J_{C,H}$ value with a maximum for the conformation in which the O–CH_3 bond is eclipsed with the other C–H bond. The values of $^1J_{C,H}$ on rotation about the CH_2–O bond depend on the conformation about the second CH_2–O bond. The absolute maximum of 162.8 Hz for $(\varphi^{H\text{-}1},\varphi^{H\text{-}1'}) = (240°,120°)$ corresponds to the conformation in which each O–CH_3 bond is eclipsed with a C–H bond of the methylene group. However, for **1**, this conformation is inaccessible.

Conformational analysis of **1** revealed seven minima for rotation about the CH_2–O bonds[18,19] which, for reasons of symmetry, correspond to the three conformers gg ($\varphi_1 = 60°,\varphi_{1'} = 60°$), gt (60°,180°), and tt (180°,180°). The gg conformer is two-fold and the gt conformer is four-fold degenerate. The calculated ratios[18] gg:gt:tt are 75.8:24.1:0.1. Simple conformational averaging based on the above population of conformers gave the value 156.4 Hz for $<^1J_{C,H}>$. The magnitude of the calculated $^1J_{C,H}$ is ~5 Hz smaller than the experimental value[20] of 162.1 Hz measured for dimethoxyethane, $CH_3CH(OCH_3)_2$. Analysis of results shows that the calculated $^1J_{C,H}$ value for **1** is 151–153 Hz when hydrogen is *gauche* to two oxygen lone-pairs [conformation at $(\varphi^{H\text{-}1},\varphi^{H\text{-}1'}) = (60°,60°)$, (60°,300°), (300°,60°), and (300°,300°) and 156–158 Hz when hydrogen is *gauche* to three oxygen lone-pairs [conformations at $(\varphi^{H\text{-}1},\varphi^{H\text{-}1'}) =$ (60°,180°), (180°,60°), (180°,300°), and (300°,180°)]. The hydrogen atom is *gauche* to four oxygen lone-pairs at $(\varphi^{H\text{-}1},\varphi^{H\text{-}1'}) = (180°,180°)$ and $^1J_{C,H}$ is ~ 161 Hz. These values are ~5 Hz smaller than those found for rigid molecules[1–3], but the conformational dependence appears to be reproduced adequately.

(b) 2-Methoxytetrahydropyran (**2**). — The calculated $^1J_{C,H}$ values at the anomeric carbon atoms of **2a** and **2e**, which were based on the INDO–FPT method and the PCILO (Perturbative Configuration Interaction with Localized Orbitals) geometrical parameters, are plotted as a function of φ^H (H–C–O–C) and ψ^H (C–O–C–H) in Figs. 2 and 3; φ^H is related to φ (O–C–O–C) by the relationship $\varphi^H = \varphi + 120°$ for **2e** and $\varphi^H = \varphi - 120°$ for **2a**. A 120° periodicity of the calculated anomeric $^1J_{C,H}$ values on ψ in Figs. 2 and 3 is based on the symmetry on rotating the methyl group. The ranges of the calculated values of $^1J_{C,H}$ for **2e** and **2a** overlap, and are 145–160 Hz, and 149–166 Hz, respectively. Thus, the application of $^1J_{C,H}$ values for diagnosing anomeric configuration may lead to errors. Clearly, the anomeric $^1J_{C,H}$ values for some conformations of **2e** are larger than for **2a** and the calculated and experimental results in representative systems do not agree. Unfortunately, there are few experimental data for **2** that can be compared with the calculated results. For example, values of 155–159 Hz were reported[21] for axial anomeric C–H bonds in substituted 2-methoxytetrahydropyrans, in comparison with values of 161–165 Hz for equatorial bonds.

The PCILO calculations[22,23] revealed two minima for rotation around the C–O bond in **2a** at φ^H 297° and 32°. The ratio of these conformers for a solution in

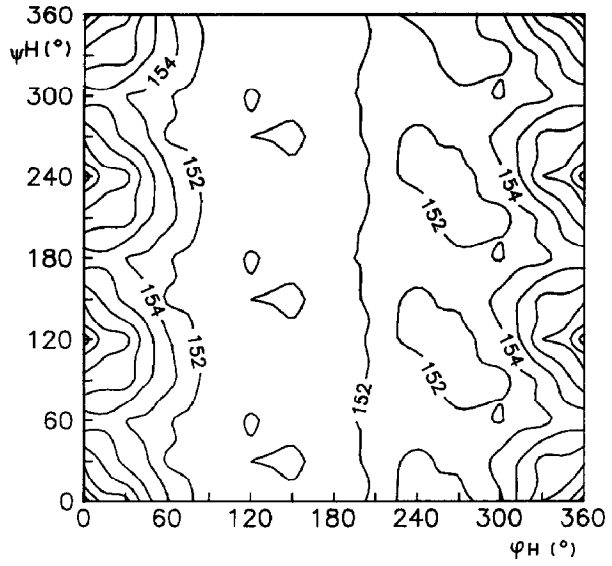

Fig. 2. Contours of the calculated INDO–FPT results for the $^1J_{C,H}$ values (Hz) at the anomeric carbon atom of 2-methoxytetrahydropyran with MeO axial (**2a**) as a function of φ^H and ψ^H.

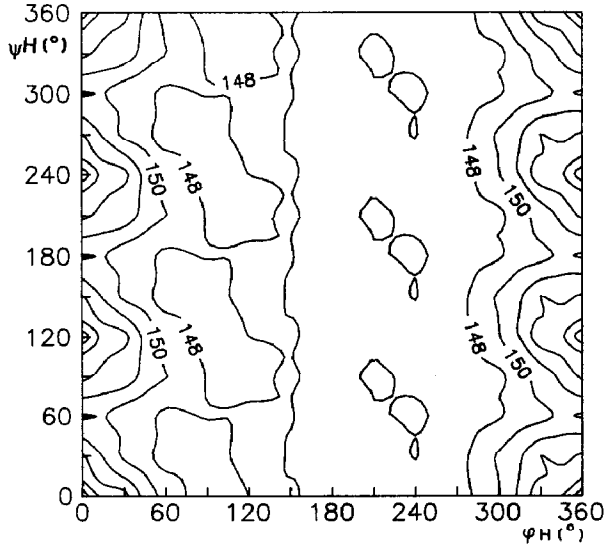

Fig. 3. Contours of the calculated INDO–FPT results for the $^1J_{C,H}$ values (Hz) at the anomeric carbon atom of 2-methoxytetrahydropyran with MeO equatorial (**2e**) as a function of φ^H and ψ^H.

chloroform[17] was 89.7:10.3. For **2e**, three minima occur at φ^H 62°, 164°, and 320°. The abundance of these conformers in solution in chloroform[17] was 82.6%, 9.2%, and 8.2%, respectively. Conformational averaging, based on the abundance of these conformers, and the corresponding INDO-FPT $^1J_{C,H}$ values, gave $<^1J_{C,H}>$ values of 148 Hz for **2e** and 156 Hz for **2a**. Thus, calculations predict correctly that an equatorial hydrogen gives a larger $^1J_{C,H}$ value than an axial hydrogen. The magnitudes of the calculated $^1J_{C,H}$ values were ~5 Hz smaller than the experimental values of 153.3 Hz in 2-methoxy-6-methyltetrahydropyran and 161.1 Hz in 2-methoxytetrahydropyran, measured for solutions in chloroform[21]. The calculated dependence of $^1J_{C,H}$ on configuration at the anomeric carbon atom and, therefore, on the orientations of ring oxygen lone-pairs, is similar to the dependence observed in **1**. The dependence of the $^1J_{C,H}$ values on φ^H predicted from calculation is different in both molecules and probably reflects the differences in the structures. Another factor that could influence the magnitude of the $^1J_{C,H}$ value is the electronegativity of the anomeric substituent (carbon versus hydrogen).

The anomeric hydrogen is *gauche* to the two ring oxygen lone-pairs in **2a** and *gauche* to one lone-pair in **2e**. The calculated $^1J_{C,H}$ value for **2e** is 152–155 Hz when one additional anomeric oxygen lone-pair is *gauche* to anomeric hydrogen (conformations at φ^H 60° and 300°) and ~149 Hz when hydrogen is *gauche* to further two anomeric oxygen lone-pairs at φ^H 180°. The two lone-pair orbitals on oxygen are delocalized by through-bond and through-space mechanisms. The electron transfer associated with these interactions depends[24,25] on the conformation about the internal C–O bonds and explains the relationship of bond lengths and bond angles to dihedral angles and, therefore, to the changes in the bond angles and bond lengths observed between anomers. The difference in the *s*-character of the C–H bond is considered also to be a consequence of the conformational dependence of the lone-pair delocalization into the antibonding orbital of the C–H bond. Therefore, the variation in $^1J_{C,H}$ values is a manifestation of the anomeric and exo-anomeric effects.

The conformational dependence of the $^1J_{C,H}$ values on φ^H in **1** and **2**, plotted in Fig. 4, can be represented satisfactorily by equation *2*, which is in the form of a truncated Fourier series.

$$^1J_{C,H} = V_1(1-\cos\varphi^H) + V_2(1\text{-}\cos2\varphi^H) + V_3(1-\cos3\varphi^H) + V_4\sin\varphi^H + V_5\sin2\varphi^H + V_6. \quad (2)$$

The calculated constants V_i are given in Table I. The main difference between the calculated and experimental $^1J_{C,H}$ values seems to be associated with the constant V_6. A source of discrepancy may be the integral parametrization and/or the neglect of the effects of electron correlation in the semiempirical description of $^1J_{C,H}$. Therefore, the shift of all of the values by a constant amount is a plausible procedure. Indeed, the addition of ~5 Hz gives values of V_6 of 169.8 Hz for **2a** and 164.1 Hz for **2e** in equation *2* (Table I) and leads to reasonable agreement with the experimental values.

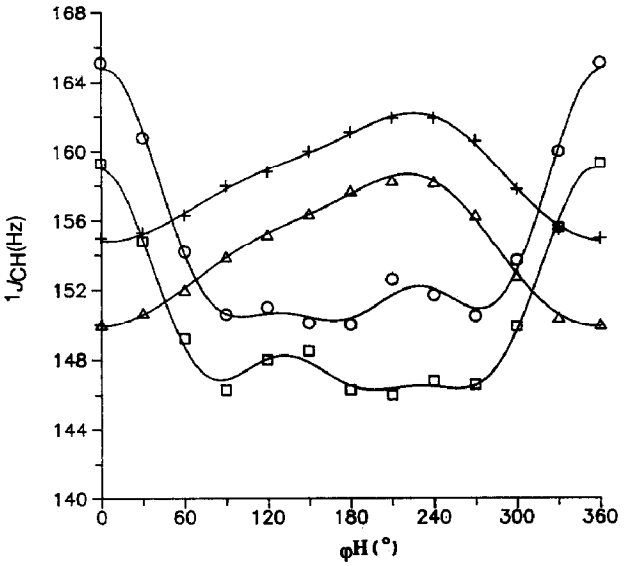

Fig. 4. A plot of the calculated INDO–FPT results for the $^1J_{C,H}$ values (Hz) for dimethoxymethane (**1**) as a function of $\varphi^{H\text{-}1}$ with $\varphi^{H\text{-}1'}$ fixed at 300° (+) and 180° (△), and for 2-methoxytetrahydropyran as a function of the dihedral angle φ^{H} with the methoxy group axial (**2a**, ○) and equatorial (**2e**, □).

TABLE I

Calculated V_i (Hz) constants of equation *2* for dimethoxymethane (**1**) and 2-methoxytetrahydropyran (**2**)

Compound	V_1	V_2	V_3	V_4	V_5	V_6
1, $\varphi^{H\text{-}1'}$ 300°	4.0	0.6	−0.1	−1.1	0.6	149.9
1, $\varphi^{H\text{-}1'}$ 180°	3.2	0.6	−0.1	−1.3	0.5	154.8
2e	−4.8	−3.0	−1.5	0.2	−0.8	159.1
2a	−5.6	−3.4	−1.7	−0.2	0.7	164.8

Molecular orbital description of the conformational dependence of $^3J_{C,H}$ *values.* — (*a*) *Dimethoxymethane* (**1**). The $^3J_{C,H}$ values between the carbon atom of the methyl group and hydrogen atoms of the methylene group ($\varphi^{H\text{-}1}$) were calculated at intervals of 30° for $\varphi^{H\text{-}1}$ and $\varphi^{H\text{-}1'}$. Inspection of the calculated data indicates that the orientation of the other methyl group ($\varphi^{H\text{-}1'}$) has little effect on the calculated values of $^3J_{C,H}$ where $\varphi^{H\text{-}1}$ is $< 120°$. The values for **1** differ by < 0.4 Hz. Exceptions are when $\varphi^{H\text{-}1}$ is 120°–180° and 200°–270°, where the effects of the conformation of the methyl group are substantial; *e.g.*, $^3J_{C,H}$ at ($\varphi^{H\text{-}1}$,$\varphi^{H\text{-}1'}$) = (150°,60°) is ~2 Hz less than the value for conformation (150°,270°). A rationalization of the decrease in the calculated $^3J_{C,H}$ values on the orientation of the other methyl group can be based on a description of oxygen lone-pair delocalization into the central methylene group. Quantitative MO analysis of lone-pair delocalization in **1** showed[24,25] that the conformational dependence of the delocalization has a two-fold symmetry with maxima at the *trans* and *cis* arrangements of the

O–C–O–C segment ($\varphi^{H\text{-}1'}$ 60°) and a minimum at the orthogonal arrangement ($\varphi^{H\text{-}1'}$ 330°). Since the electron-withdrawing character of the methoxy substituent increases with a decrease of the oxygen lone-pair delocalization, the rotation from the *trans* position should lead to an increase in the magnitude of coupling constant.

The calculated $^3J_{C,H}$ values for **1** follow the angular dependence, measured about the C–O bond, shown in equation *3*.

$$^3J_{C,H} = A\cos^2\varphi^H + B\cos\varphi^H + C + D\sin\varphi^H + E\sin 2\varphi^H, \quad (3)$$

in which $^3J_{C,H}$ ($\varphi^H = 180°$) is $> {}^3J_{C,H}(0°)$, and $^3J_{C,H}$ (90°) is 0°. In order to take into consideration the lack of the 180° periodicity, the sin terms were added to the Karplus dependence. The range of values of $^3J_{C,H}$ in **1** is ~11 Hz, depending on $\varphi^{H\text{-}1'}$. When $\varphi^{H\text{-}1'}$ is 180°, the calculated results are reproduced to within ~0.1 Hz by equation *3* where A – E are 7.1, −2.4, −0.1, −0.4, and 0.7 Hz, respectively. When $\varphi^{H\text{-}1'}$ is 300°, A–E are 7.5, −2.4, −0.2, −0.3, and 0.5 Hz, respectively. The A–E values 7.3, −2.4, −0.1, −0.3, and 0.6 Hz, respectively, were obtained based from both sets of data.

The INDO FPT results for the $^3J_{C,H}$ values and those calculated from equation *3* for **1** are plotted in Fig. 5 as a function of $\varphi^{H\text{-}1}$. The effect on the $^3J_{C,H}$ value due to different orientations of the second methyl group, for $\varphi^{H\text{-}1'}$ of 180° and 60°, is negligible and the calculated values when $\varphi^{H\text{-}1}$ is 180° are asymmetric, which is reflected in the values of the sin terms. This lack of symmetry, which ranges from 0.3 to 1.5 Hz, is attributable to the large difference in electronegativity of the central carbon substituents (hydrogen versus oxygen). The magnitude of the $^3J_{C,H}$ value is larger when the methyl group is oriented on the side of the hydrogen atom. The calculated average value

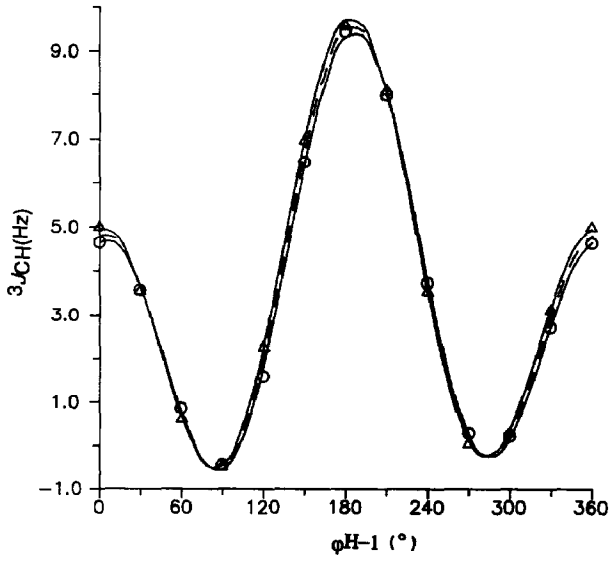

Fig. 5. A plot of the calculated INDO–FPT results for the $^3J_{C,H}$ values (Hz) for dimethoxymethane (**1**) as a function of $\varphi^{H\text{-}1}$ (---), and for dimethoxymethane with $\varphi^{H\text{-}1'}$ fixed at the 300° (△) and 180° (○) position.

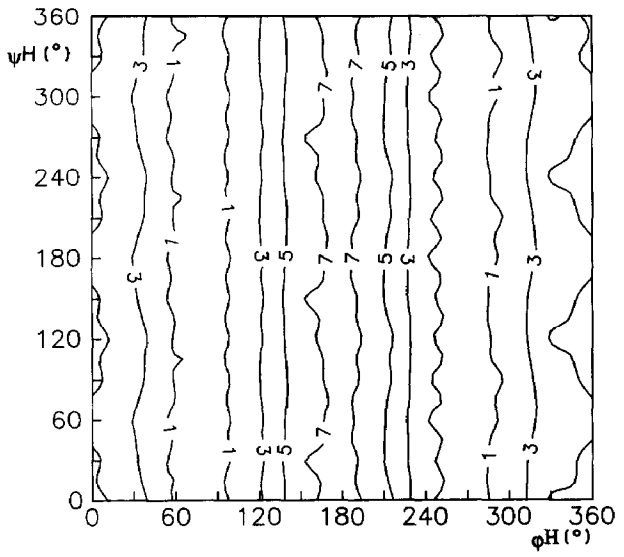

Fig. 6. Contours of the calculated INDO–FPT results for J^{ψ} (Hz) between the anomeric hydrogen and methyl carbon in 2-methoxytetrahydropyran with MeO equatorial (**2e**), as a function of φ^{H} and ψ^{H}.

$<^{3}J_{C,H}>$ is 5.4 Hz, based on the simple assumption of the average of the stable conformations, is ~1 Hz smaller than those observed. However, in flexible molecules, the consistently smaller values for the average values are expected on the basis of the above approach and it is more appropriate to weight the values with the internal barriers.

(*b*) *2-Methoxytetrahydropyran* (**2**). Two $^{3}J_{C,H}$ values were calculated for each anomer, namely, J^{φ} for φ^{H} and J^{ψ} for ψ^{H}. These angles describe the mutual orientation of contiguous residues in oligosaccharides. The plot of J^{ψ} for **2e** as a function of φ^{H} and ψ^{H} in Fig. 6 demonstrates the small effect of the rotation about the neighboring C–O bond on the value of $^{3}J_{C,H}$. The 120° periodicity of the maps in the ψ^{H} direction arises from the symmetry associated with rotation of the methyl group as mentioned above.

The rotation influences the value of $^{3}J_{C,H}$ substantially in the proximity of the barrier at a dihedral angle of 0° (the change is ~1.5 Hz), in the proximity of the barrier at 180° the variation is ~1 Hz, and for other angles the effects are smaller. The decrease may be ascribed to the γ-substituent effect associated with non-bonded interactions of the anomeric hydrogen and hydrogens of the methyl group. Comparison of the data for **2** and **1** shows that substitution of hydrogen by a ring carbon atom at the anomeric carbon of **1** lowers the magnitude of the calculated $^{3}J_{C,H}$ value and restores the 180° periodicity of the curve. A rationalization of the decrease in the calculated values can be based, as for a C–C–C–H segment, on the greater electronegativity of the methylene group than of hydrogen[26]. The calculated values of $^{3}J_{C,H}$ are 0–9 Hz for **2e** and 0–8 Hz for **2a**, whereas a maximum of 11 Hz at $(\varphi^{H\text{-}1},\varphi^{H\text{-}1'}) = (180°,180°)$ is predicted for **1**.

TABLE II

Calculated constants (Hz) of equation *3* for 2-methoxytetrahydropyran (**2**)

Compound	*Angle*	*A*	*B*	*C*
2e	φ^H	6.3	−1.1	−0.1
	ψ^H	6.2	−1.2	0.1
2a	φ^H	6.5	−1.4	−0.2
	ψ^H	6.1	−1.2	0.1
2		6.3	−1.2	0.1

Unfortunately, there are no experimental $^3J_{C,H}$ values which can be used for comparison. However, the reliability of the computed conformational dependence can be compared with experimental values obtained for carbohydrate derivatives which show conformational dependence expressed by equation *1*. The INDO–FPT calculated results for J^φ and J^ψ of **2** can be represented generally to better than 0.2 Hz by the first three terms of equation *3*, and the corresponding constants A–C are given in Table II. The calculated constants reflect the effect of configuration at the anomeric centre, which was already inferred from the results calculated above for **1**. The correspondence between the conformational dependences of J^φ and J^ψ supports the suggestion that the same equation could be used to describe the angular dependence of $^3J_{C,H}$ value around the C–O glycosidic bonds.

Since equation *1* is based on the saccharide derivatives that have different orientations around the ring C–O bond, the overall dependence of $^3J_{C,H}$ on dihedral angle was calculated as a superposition of the J^φ and J^ψ dependences. The resulting dependence has the form

$$^3J_{C,H} = 6.3\cos^2\varphi^H - 1.2\cos\varphi^H + 0.1. \quad (4)$$

The correspondence between calculated and experimental dependence of $^3J_{C,H}$ described by equations *1* and *4* is reasonably good, especially when a decrease in the magnitude of the $^3J_{C,H}$ value in carbohydrates relative to **2**, due to the substituents effects, can be expected.

Thus, the values of $^1J_{C,H}$ and $^3J_{C,H}$ depend on the dihedral angles about the glycosidic C–O bonds. In the calculations on the model compounds **1** and **2**, this variation may be as much as 21 Hz for $^1J_{C,H}$ and 11 Hz for $^3J_{C,H}$. Where experimental data are available, the agreement between calculated and experimental data is satisfactory and suggests that both coupling constants may complement other types of n.m.r. parameters as probes of oligosaccharide structure in solution. It is important to include the effects of conformational averaging in such applications. Although it appears likely that $^1J_{C,H}$ values can provide useful information on the structure of oligosaccharides in solution, the above results were obtained on model compounds and the effect of electronegative ring substituents and geometry were not investigated. However, preliminary results on oligosaccharides[27] indicate that such a relationship may be established.

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