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One-bond carbon–proton coupling constants: angular dependence in α-linked oligosaccharides*

Igor Tvaroska[†]
Institute of Chemistry, Slovak Academy of Sciences, 84238 Bratislava (Czechoslovakia)
and François R. Taravel
Centre de Recherches sur les Macromolécules Végétales, C.N.R.S., B.P. 53X, 38041 Grenoble (France)

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ABSTRACT

An investigation is presented of the angular dependence of $^1J_{C,H}$ in model compounds related to α-linked oligosaccharides. Values calculated by FPT formulation in the semi-empirical INDO method for models of (1→1)-, (1→2)-, (1→3)-, and (1→4)-linked disaccharides were compared, and the effect of the orientation of HO-2 was elucidated. The angular dependence of $^1J_{C,H}$ on the glycosidic dihedral angles Φ^H and Ψ^H was characterised in the form $^1J_{C,H} = A \cos 2\phi + B \cos \phi + C \sin 2\phi + D \sin \phi + E$. The $^1J_{C,H}$ values, measured by DEPT methods for C-1–H-1 and C-X′–H-X′ in various rigid carbohydrates, were used to adjust the calculated angular dependences and to determine solvent effects. Based on the abundance of the conformers for maltose and isomaltose, the thermodynamically averaged $^1J_{C,H}$ values have been calculated. The results obtained ($<^1J_{C\text{-}1,H\text{-}1}>$ 169.9, $<^1J_{C\text{-}4',H\text{-}4'}>$ 147.7 Hz for methyl β-maltoside and $<^1J_{C\text{-}1,H\text{-}1}>$ 169.8 Hz for methyl β-isomaltoside) agree with the experimental values of 172.4, 147.7, and 170.3 Hz, respectively.

INTRODUCTION

The potential of $J_{C,H}$ values for the elucidation of conformations is well known and several empirical correlations have been established[1,2]. For carbohydrates, the $^1J_{C,H}$ and $^3J_{C,H}$ values that involve the anomeric carbon are the most important. $^3J_{C,H}$ values for oligosaccharides[3–16] have been studied intensively and parameters for the angular dependence in C–O–C–H bond fragments based on rigid carbohydrates have been published[15,16]. The $^1J_{C,H}$ values were used primarily to determine anomeric configurations.

We have investigated the dependence on conformation of $^1J_{C,H}$ in model compounds related to glycosides[17] and in the (1→4)-linked disaccharide glycosides[18], methyl β-xylobioside, methyl β-cellobioside, and methyl α-xylobioside, using the finite perturbation theory (FPT) for nuclear spin–spin coupling constants in the intermediate neglect of differential overlap (INDO) approximation of semi-empirical molecular orbital (MO) theory[19]. These studies showed that the values of $J_{C\text{-}1,H\text{-}1}$ and $J_{C\text{-}4',H\text{-}4'}$ vary

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[†] To whom correspondence should be addressed.

characteristically with the dihedral angles about C–O bonds, and, for disaccharides, this variation may be as much as 11 Hz. In addition to calculated ${}^1J_{C,H}$ values, the values of ${}^1J_{C,H}$ were measured[18] for cyclomaltohexaose (αCD) and methyl β-cellobioside in order to provide data for well-defined conformations in solution. This action was necessary since the FPT–INDO method underestimates the absolute values of ${}^1J_{C,H}$, whereas the dependence on conformation appears to be reproduced adequately[17]. With the help of these experimental values, the angular dependence was expressed in the form

$$ {}^1J_{C,H} = A\cos 2\phi + B\cos\phi + C\sin 2\phi + D\sin\phi + E, $$

with different values of the constants A–E for the α and β anomers. These relationships between ${}^1J_{C,H}$ and the glycosidic dihedral angles were also used to predict $<{}^1J_{C\text{-}1,H\text{-}1}>$ and $<{}^1J_{C\text{-}4',H\text{-}4'}>$ for methyl β-xylobioside.

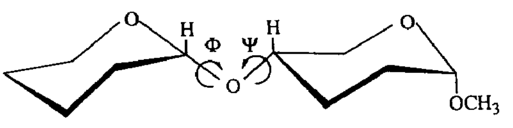
However, the derived equations were based[18] on experimental data for only two disaccharides, and only limited information was available on the influence of the structure and of the pattern of substitution. We now report an extension of this work to other model systems.

EXPERIMENTAL

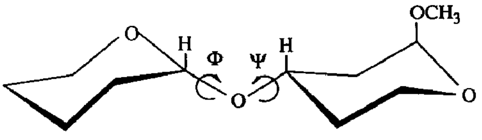
General. — The dependence of ${}^1J_{C,H}$ on Φ^H and Ψ^H studied for 2-methoxy-5- (**1a**), -4- (**2a**), -3- (**3a**), and 2-(tetrahydropyran-2-yloxy)tetrahydropyran (**4a**), which represent α-(1→4)-, α-(1→3)-, α-(1→2)-, and α-(1→1)-linked disaccharides, respectively, and **5a** and **6a** which are 3-hydroxy derivatives of **1a** related to α-(1→4)-linked disaccharides with the D- and L-*glycero* configurations at C-2. The geometries of **1a**–**6a** were based on the optimised geometry of 2-methoxytetrahydropyran[20]. A value of 115° was used for the C–O–C glycosidic bond angle. An exception was the investigation of the effect of the C–O–C bond angle on ${}^1J_{C,H}$, where values of 112° and 118° were also used. The ${}^1J_{C,H}$ values were calculated by the FPT–INDO–MO method[19].

The following known compounds were chosen to provide H–C–O–C–H fragments with well-defined conformations in solution: α,α-trehalose (**7**), 1,6-anhydro-β-D-glucopyranose (**8**), 2,3,4-tri-*O*-acetyl-1,6-anhydro-β-D-glucopyranose (**9**), 2,3-di-*O*-acetyl-1,6-anhydro-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-β-D-glucopyranose (**10**), cyclomalto-hexaose (αCD, **11**), -heptaose (βCD, **12**), and -octaose (γCD, **13**), 1,6:2,3-dianhydro-4-*O*-benzyl-β-D-mannopyranose[21] (**14**), methyl β-isomaltoside (**16**), and methyl β-maltoside (**15**).

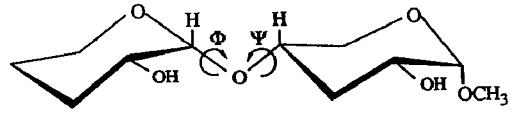
Purified compounds were each dissolved (4%) in the appropriate solvent [D_2O, $(CD_3)_2SO$, dioxane-d_8, pyridine-d_5, or $CDCl_3$]. Coupling constants were determined from spectra measured at 30° with a Bruker AM 400 spectrometer equipped with an Aspect 3000 computer process controller. DEPT experiments with polarisation transfer from ${}^1H$ to ${}^{13}C$ nuclei for refocussed ${}^1H$-coupled spectra were used. The values given are ±0.5 Hz.



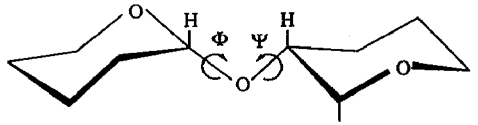
1a



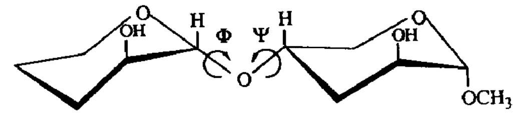
2a



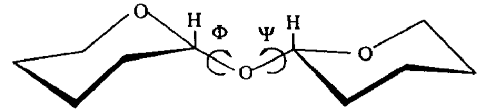
5a



3a



6a



4a

RESULTS AND DISCUSSION

MO description of the dependence of $^1J_{C,H}$ on conformation involving the anomeric centre. — The calculated INDO–FPT $^1J_{C\text{-}1,H\text{-}1}$ values are expressed as 2D Φ^H and Ψ^H maps where the torsional angles Φ^H (H-1–C-1–O-X′–C-X′) and Ψ^H (C-1–O-X′–C-X′–H-X′) describe the relative orientation of the monosaccharide residues. The 2D maps were prepared by rotating the rigid residue to each combination of Φ^H and Ψ^H on a 30° grid and evaluating the $^1J_{C,H}$ value.

The results calculated for (1→4)-linked molecules are plotted in Fig. 1. The map calculated for **6a** was similar to that for **5a** and is not shown. Comparison of the maps for **1a**, **5a**, and **6a** showed that the effect of orientation of the 2-substituent in the α anomers was small and that the main features were similar. The calculated values were in the range of 130–150 Hz. The lowest $J_{C\text{-}1,H\text{-}1}$ values were found for Φ^H 60° and 270°. The maximum values correspond to orientations between 150–180°. Whereas the $J_{C\text{-}1,H\text{-}1}$ values for Φ^H 90–270° imply that they do not depend on the value of Ψ^H, the values for Φ^H ~0° depend on Ψ^H. The higher $^1J_{C,H}$ values were observed for Ψ^H 120° and 240°. The main reasons for this behaviour are steric interactions of the C-1–H-1 bond and atoms of the aglycon. The $^1J_{C,H}$ values in these conformations do not correspond to any physical situation, as the energies are in excess of those required to distort the molecule. Therefore, the $^1J_{C,H}$ values calculated for such conformers are either very large or small and were discarded in further study. These findings are supported by the investigation of the effect of the magnitude of the glycosidic angle (τ) on the $^1J_{C,H}$ values shown in Fig. 1, where maps with τ 112° (Fig. 1c) and 118° (Fig. 1d) are compared and show clearly how the steric interactions limit the applicability of the FPT–INDO method for the calculation of the $^1J_{C,H}$ values. In the map where τ is 112°, the strong steric interactions

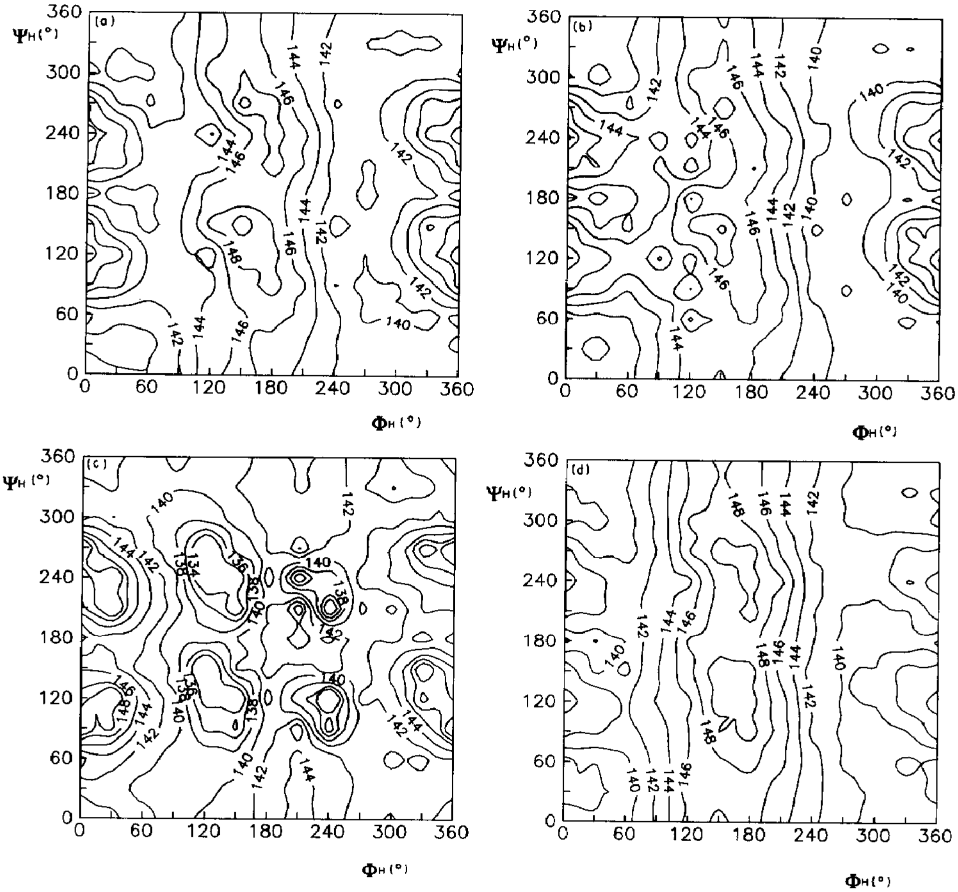


Fig. 1. Contours of the calculated FPT–INDO results for the $J_{\text{C-1,H-1}}$ values (Hz) for the α-(1→4)-linked oligosaccharide models as a function of Φ^{H} and Ψ^{H}: (*a*) for **1a** (τ 115°), (*b*) **5a** (τ 115°), (*c*) **1a** (τ 112°), (*d*) **1a** (τ 118°).

determine the ${}^1J_{\text{C,H}}$ values and therefore the general shape of the map. As can be seen in the map where τ is 118°, the dependence of the ${}^1J_{\text{C,H}}$ values on Ψ^{H} is smaller than when τ is 115° (Fig. 1a).

The magnitude of ${}^1J_{\text{C,H}}$ varies markedly[1,2] with the *s*-character of the C–H bond, which is influenced by the electronegativity of the substituent, bond angle, *etc*. The orientation of the lone pairs on oxygen has been used also to explain[22,24] differences in the ${}^1J_{\text{C-1,H-1}}$ values relative to axial and equatorial H-1.

The electron distribution at the anomeric centre is strongly influenced by interactions that involve the lone pairs of electrons and are reflected in the anomeric and exo-anomeric effects[25]. The two lone pairs on oxygen are delocalised by through-bond and through-space mechanisms[26], and electron transfer associated with these interactions depends on the conformation about the internal C–O bonds. Since the variation in the *s*-character of the C–H bond is also a consequence of the dependence on conformation of the delocalisation of the lone pairs into the antibonding orbital of the C-1–H-1 bond, it has been suggested[17] that the variation in $J_{C\text{-}1,H\text{-}1}$ is a manifestation of the anomeric and exo-anomeric effects. For the α-linked oligosaccharides, the orientation of lone pairs on the ring oxygen with respect to the C-1–H-1 bond remains fixed. The small variations due to the flexibility of the chair form of a pyranoid ring may be neglected. In contrast, the orientations of the lone pairs on O-1 with respect to the C-1–H-1 bond vary with the rotation about the C-1–O-1 bond, which may be assumed to be a main factor that determines the conformational dependence of $J_{C\text{-}1,H\text{-}1}$.

The magnitude of the delocalisation interactions depends on the mutual orientation of pertinent orbitals and their energies. Since C-1 is linked to the ring oxygen O-5, the energy of the antibonding orbital of the C-1–H-1 bond is lower than that of the aglycon C–H bond. Therefore, the delocalisation of the lone pairs into this region is significantly lower than at the anomeric centre. Moreover, the influence of these interactions on the energy of lone pairs of O-1 is small. There are two qualitative consequences of these interactions. First, since the delocalisation interactions into the C–H bond are influenced only marginally by variation of Ψ^H, $J_{C\text{-}1,H\text{-}1}$ might be expected to depend on Ψ^H only slightly. Second, since the magnitude of the delocalisation interactions into the aglycon C–H bond is lower than into the C-1–H-1 bond, the angular dependence of $^1J_{C\text{-}X',H\text{-}X'}$ should be smaller in comparison with that of $J_{C\text{-}1,H\text{-}1}$.

Figure 2 shows the contour maps of $J_{C\text{-}1,H\text{-}1}$ calculated for (1→3)- and (1→2)-linked compounds **2a** and **3a**, respectively. Comparison of the former map with that for **1a** (Fig. 1a) revealed the main features to be similar. However, the magnitude of $J_{C\text{-}1,H\text{-}1}$ for an antiperiplanar (*ap*) orientation about the C-1–O-1 bond is slightly higher. The shape of the map for **3a** is completely different, the contours being influenced by steric interactions of MeO-1 and the C-1–H-1 bond.

The aglycon C–H bond. — The calculated $^1J_{C\text{-}X',H\text{-}X'}$ values for **1a**–**6a** are ~20 Hz lower than those of $J_{C\text{-}1,H\text{-}1}$ and a variation of 117–130 Hz was observed. The dependence of $^1J_{C\text{-}X',H\text{-}X'}$ on conformation is comparable in all of the molecules studied. This situation

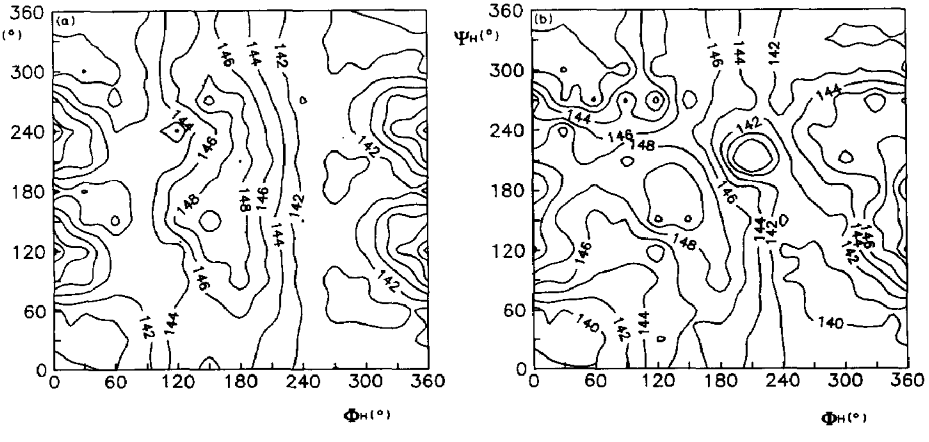


Fig. 2. Contours of the calculated FPT–INDO results for the $J_{C\text{-}1,H\text{-}1}$ values (Hz) of (*a*) the α-(1→3)-linked molecule **2a** and (*b*) the α-(1→2)-linked molecule **3a**.

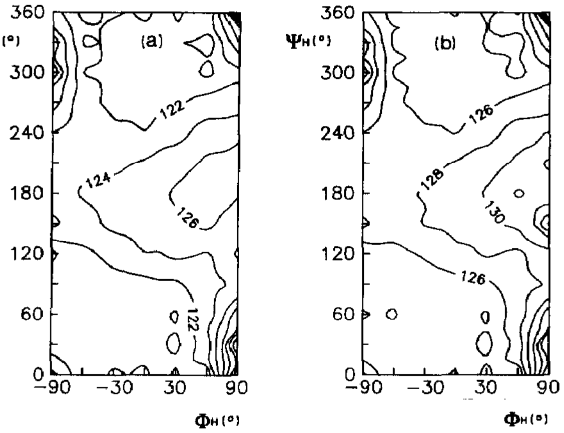


Fig. 3. Contours of the calculated FPT–INDO results for the ${}^1J_{\text{C-X}',\text{H-X}'}$ values (Hz) of (*a*) the α-(1→4)-linked molecule **1a** and (*b*) the α-(1→3)-linked molecule **2a**.

is illustrated in Fig. 3 where the contours of ${}^1J_{\text{C-X}',\text{H-X}'}$ for the α-(1→4)-linked molecule **1a** and the (1→3)-linked molecule **2a** are plotted. Since, for values of Φ between 90° and 270°, the ${}^1J_{\text{C,H}}$ values were influenced strongly by the proximity of the C–H bond and atoms of the ring, the FPT–INDO method failed to predict reasonable magnitudes of ${}^1J_{\text{C,H}}$ and the calculated values were discarded. Therefore, the ${}^1J_{\text{C,H}}$ values were rearranged under the shape shown in Fig. 3. In agreement with the qualitative discussion on the role of the lone pair on the magnitude of ${}^1J_{\text{C,H}}$, the variation of ${}^1J_{\text{C-X}',\text{H-X}'}$ for an individual molecule is lower (by ~6 Hz) than that of $J_{\text{C-1,H-1}}$. As can be seen from Fig. 3, the main features for both maps are preserved, but the magnitudes of $J_{\text{C-3}',\text{H-3}'}$ are larger (~2 Hz) than those of $J_{\text{C-4}',\text{H-4}'}$. In contrast, the calculated values of $J_{\text{C-2}',\text{H-2}'}$ are ~1 Hz lower than those of $J_{\text{C-4}',\text{H-4}'}$, although the dependences are comparable.

The angular dependence of ${}^1J_{C,H}$. — The calculated ${}^1J_{\text{C,H}}$ values were used to establish the angular dependence on the torsion H–C–O–C angle in the form:

$$ {}^1J_{\text{C,H}} = \text{A} \cos 2\Phi^{\text{H}} + \text{B} \cos \Phi^{\text{H}} + \text{C} \sin 2\Phi^{\text{H}} + \text{D} \sin \Phi^{\text{H}} + \text{E}. \qquad (1) $$

The sine terms of the above Fourier series account for the asymmetry of the dependence introduced by the substituent. Because of the steric interactions, 50 to 106 calculated ${}^1J_{\text{C,H}}$ values were used to derive the constants A–E in eq. *1* [for the (1→1)-linked molecule, the number of points was 32]. The data were fitted by the program COMPLEX[27] to a curve of the form described by eq. *1*. The resulting curves for the selected compounds are shown in Figs. 4 and 5, and the constants are listed in Tables I and II. The mean values for (1→4)-linked molecules and all molecules except the (1→1)-linked model (**4a**) are also included. The magnitude of the C–O–C glycosidic bond angle is frequently >115°. In order to take this into account, the data where τ is 118° were considered in calculating the mean values. As can be seen, the angular dependence of ${}^1J_{\text{C,H}}$ on Φ^{H} is similar for all types of linkages. The exception is the α-(1→1) linkage in **4a**, a symmetrical molecule that represents a non-reducing disaccharide. The electron distribution is influenced strongly by the interactions of the lone pairs in the C–O–C–O–C–O–C segment, which is not present in any other of the molecules studied. The calculated constants A = 0.99, B = −4.08, C = −0.13, and D = 0.72 for $J_{C\text{-}1,H\text{-}1}$, and A = 0.91, B = −2.57, C = −0.01, and D = 0.32 for $J_{C\text{-}4',H\text{-}4'}$, based only on methyl α-xylobioside[18], are in good agreement with those in Tables I and II. Thus, the mean angular dependences of ${}^1J_{C,H}$, taking into account also the values of A–D for methyl α-xylobioside[18], may be expressed in the forms:

$$
\begin{aligned}
{}^1J_{C\text{-}1,H\text{-}1} &= 1.32\cos 2\Phi^H - 3.38\cos\Phi^H - 1.05\sin 2\Phi^H + 1.27\sin\Phi^H + 142.39, (2)\\
{}^1J_{C\text{-}X',H\text{-}X'} &= 1.02\cos 2\Psi^H - 1.81\cos\Psi^H - 0.19\sin 2\Psi^H + 0.41\sin\Psi^H + 123.16, (3)
\end{aligned}
$$

and, for a (1→1) linkage,

$$
{}^1J_{C\text{-}1,H\text{-}1} = 0.72\cos 2\Phi^H - 2.32\cos\Phi^H - 1.20\sin 2\Phi^H + 1.27\sin\Phi^H + 142.76. (4)
$$

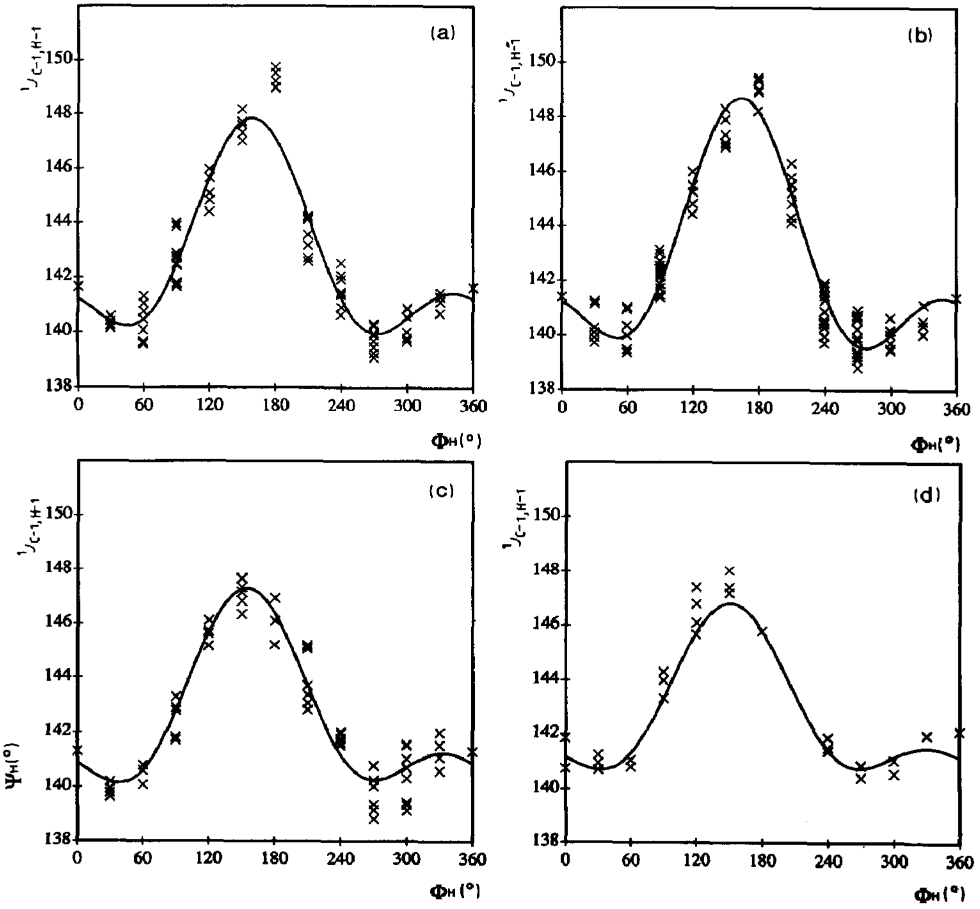


Fig. 4. The $J_{C\text{-}1,H\text{-}1}$ values (x) as a function of Φ^H for (*a*) **1a**, (*b*) **2a**, (*c*) **3a**, and (*d*) **4a**. The solid curves show the best approximation to the indicated points.

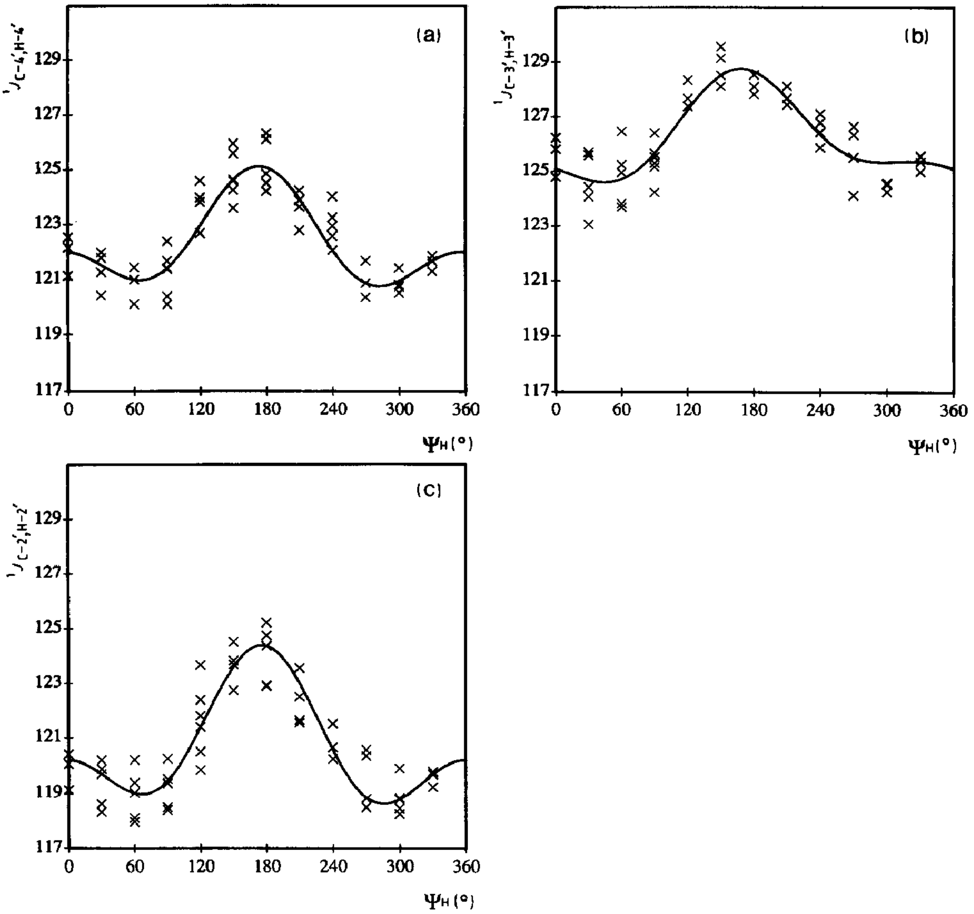


Fig. 5. The $J_{C-X',H-X'}$ values (x) as a function of Ψ^H for (*a*) **1a**, (*b*) **2a**, and (*c*) **3a**. The solid curves show the best approximation to the indicated points.

TABLE I

Calculated constants A–E (Hz) of eq. *1* for $J_{C-1,H-1}$ in **1a–6a**

Compound	*A*	*B*	*C*	*D*	*E*
1a	1.475	−2.953	−1.279	1.255	142.69
1a (τ = 118°)	1.405	−4.751	−1.024	1.321	142.56
5a	1.133	−2.865	−1.161	1.709	141.58
6a	1.202	−2.758	−1.263	1.475	141.99
2a	1.988	−3.494	−1.138	1.129	142.73
3a	1.048	−2.748	−1.329	1.260	142.58
4a	0.717	−2.318	−1.203	1.273	142.76
Mean (1→4)[a]	1.304	−3.322	−1.182	1.440	142.21
Mean (total)[b]	1.375	−3.261	−1.199	1.358	142.39

[a] For a (1→4) linkage. [b] The (1→1) linkage was not included.

TABLE II

Calculated constants A–E (Hz) of eq. *1* for $^{1}J_{C\text{-}X',H\text{-}X'}$ in **1a**–**3a**, **5a**, and **6a**

Compound	*A*	*B*	*C*	*D*	*E*
1a	1.196	−1.537	−0.245	0.269	122.34
1a (τ = 118°)	1.072	−1.548	−0.128	0.486	122.56
5a	0.850	−1.591	−0.005	1.264	122.85
6a	0.962	−1.535	−0.353	0.128	124.27
2a	0.642	−1.781	−0.442	0.075	126.24
3a	1.560	−2.077	−0.169	0.302	120.71
Mean (1→4)	1.020	−1.553	−0.183	0.537	123.01
Mean (total)	1.047	−1.678	−0.224	0.421	123.16

Previous investigations[17,18] of the dependence of $^{1}J_{C,H}$ on conformation showed that FPT–INDO underestimates the absolute $^{1}J_{C,H}$ values. Therefore, it was proposed[17] to adjust all of the $^{1}J_{C,H}$ values by a constant amount using the experimental data for molecules with well-defined conformation. An application of this approach corrects only values of E in eq. *1*. The same procedure is used in the present investigation. For this purpose, $^{1}J_{C,H}$ values were measured for several compounds and they are listed together with values for Φ^{H} and Ψ^{H} in Table III.

TABLE III

Torsional angles and measured $^{1}J_{C,H}$ values for **7**–**14**

Compound	*Array*	*Deuterated solvent*	Φ^{H}	$^{1}J_{C,H}$	$^{1}J_{C,H}$ *(vacuum)*
7	H-1–C-1–O-1′–C-1′	Water	177	172.5	169.5
8	H-1–C-1–O-6–C-6	Dioxane	144	173.2	172.5
		Pyridine		172.4	
		Methanol		173.8	
		Methyl sulfoxide		174.1	
		Water		175.8	
	H-5–C-5–O-5–C-1	Dioxane	164	156.5	155.9
		Pyridine		155.75	
		Methanol		156.7	
		Methyl sulfoxide		156.7	
		Water		158.5	
	H-6$_{exo}$–C-6–O-6–C-1	Water	107	152	149.7
	H-6$_{endo}$–C-6–O-6–C-1	Water	118	154	151.7
9	H-1–C-1–O-5–C-6	Chloroform	144	179	178.8
10	H-1–C-1–O-5–C-6	Chloroform	144	179	178.8
11	H-1–C-1–O-4′–C-4′	Water	22.3	169.6	166.3
	H-4′–C-4′–O-4′–C-1		17.3	143.9	141.6
12	H-1–C-1–O-4′–C-4′	Water	−21.3	169.3	166.3
	H-4′–C-4′–O-4′–C-1		14.2	143.5	141.2
13	H-1–C-1–O-4′–C-4′	Water	−8.3	169.4	166.4
	H-4′–C-4′–O-4′–C-1		−2.0	143.7	141.4
14	H-1–C-1–O-6–C-6	Chloroform	110	173.7	173.5

In general, spin–spin coupling constants are dependent on the solvent due to intermolecular interactions[28]. The present FPT–INDO calculation of ${}^1J_{C,H}$ does not take into account solvent effects. In order to estimate the solvent effect, $J_{C\text{-}1,H\text{-}1}$ and $J_{C\text{-}5,H\text{-}5}$ values for **8** were measured for different solvents (Table III). The solvent dependence may be represented in the linear form $J = a\,\varepsilon + b$, where a is a measure of the strength of the dielectric solvent effect on the coupling constants, and b represents the ${}^1J_{C,H}$ values for an isolated molecule. The observed ${}^1J_{C,H}$ values for **8**, shown in Fig. 6, fall on a straight line and the resulting dependences are:

$$ {}^1J_{C\text{-}1,H\text{-}1} = 0.0390\,\varepsilon + 172.53 \qquad (5) $$
$$ {}^1J_{C\text{-}5,H\text{-}5} = 0.0294\,\varepsilon + 155.86 \qquad (6) $$

The magnitudes of the constant a indicate that the solvent-induced changes of ${}^1J_{C,H}$ are larger for the C-1–H-1 bond than for the aglycon bond. Thus, the difference in ${}^1J_{C,H}$, calculated from eq. *5* and *6* for the isolated molecule ($\varepsilon = 1$) and for aqueous solution ($\varepsilon = 78.5$), is 3.02 Hz for the C-1–H-1 bond and 2.28 Hz for the C-5–H-5 bond. The application of this dependence to oligosaccharides, however, is based on the assumption that the solvent-induced electronic changes in α-linked oligosaccharides are similar to those in **8**.

The experimental values were corrected for the effect of the solvent, using eq. *5* and *6*, and compared with the corresponding ${}^1J_{C,H}$ values based on eq. *2* and *3*. The addition of the mean estimated differences (26.5 and 22.3 Hz) gives corrected values of E and these are given in the following equations (*in vacuo*):

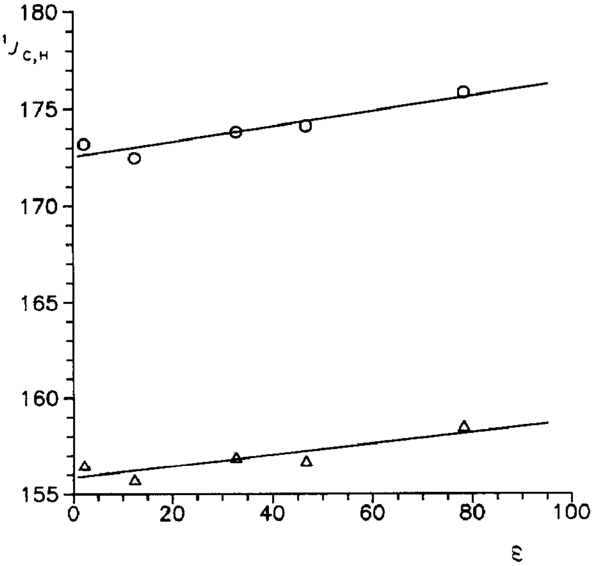


Fig. 6. Dependence of experimental $J_{C\text{-}1,H\text{-}1}$ (o) and $J_{C\text{-}5,H\text{-}5}$ (Δ) values (Hz) for 1,6-anhydro-β-D-glucopyranose (**8**) as a function of the dielectric constant (ε) of the solvent.

$$^1J_{C\text{-}1,H\text{-}1} = 1.32\cos 2\Phi^{H} - 3.38\cos\Phi^{H} - 1.05\sin 2\Phi^{H} + 1.27\sin\Phi^{H} + 168.9, \quad (7)$$
$$^1J_{C\text{-}X',H\text{-}X'} = 1.02\cos 2\Psi^{H} - 1.81\cos\Psi^{H} - 0.19\sin 2\Psi^{H} + 0.41\sin\Psi^{H} + 145.4, \quad (8)$$

and for α-(1→4)-linked oligosaccharides,

$$^1J_{C,H} = 0.72\cos 2\Phi^{H} - 2.32\cos\Phi^{H} - 1.20\sin 2\Phi^{H} + 1.27\sin\Phi^{H} + 166.4. \quad (9)$$

The experimental $^1J_{C,H}$ values for **9** and **10** are too high in comparison with that for **18**. Therefore, they were not used for the adjustment of E in eq. *2*. The higher values of $^1J_{C,H}$ might reflect the influence of acetylation. If this is true, then E for acetylated oligosaccharides in eq. 7 would be 173.9 Hz.

Combination of eqs. *5* and *6* with eqs. *7* and *8* yields the following expressions which incorporate the solvent polarity into the angular dependence of $^1J_{C,H}$:

$$^1J_{C\text{-}1,H\text{-}1} = 1.32\cos 2\Phi^{H} - 3.38\cos\Phi^{H} - 1.05\sin 2\Phi^{H} + 1.27\sin\Phi^{H} + 168.9 + 0.039\,\varepsilon, \quad (10)$$
$$^1J_{C\text{-}X',H\text{-}X'} = 1.02\cos 2\Psi^{H} - 1.81\cos\Psi^{H} - 0.19\sin 2\Psi^{H} + 0.41\sin\Psi^{H} + 145.4 + 0.0294\,\varepsilon. \quad (11)$$

Because oligosaccharides are usually flexible on the n.m.r. time scale, the observed values represent average values. Therefore, the estimation of the reliability of conformational dependences described by eqs. 7–9 requires knowledge of the conformational properties for a particular oligosaccharide. For the α linkage, the conformational equilibria have been published for maltose[29] and isomaltose[30] in aqueous solution. The calculation predicted[29] the four maltose conformers M1 (Φ^{H} −20.7, Ψ^{H} −24.2), M2 (17.5, 18.9), M3 (−65.9, −43.0), and M4 (−28.7, −167.8) in the ratios 25.7:17.5:26.3:30.5. The calculation for isomaltose[30] showed that there was an equilibrium of 11 conformers. The ratios of the conformers GG1 (Φ^{H} 33.2), GG2 (−53.1), GG3 (−48.7), GT1 (−55.4), GT2 (−51.2), GT3 (−13.1), GT5 (−30.8), GT6 (41.4), TG1 (−37.7), TG2 (52.9), and TG3 (−53.6) were 31.44:19.37:0.77:3.03:2.38:0.34:0.18: 24.68:10.58:5.55:1.65. Averaging of the conformers based on the above abundances and the $^1J_{C,H}$ values calculated using eqs. *5*–*8* gave the values $<J_{C\text{-}1,H\text{-}1}>$ 169.8 Hz and $<J_{C\text{-}4',H\text{-}4'}>$ 147.7 Hz for maltose, and $<J_{C\text{-}1,H\text{-}1}$ 169.8 for isomaltose. These values can be compared to the experimental values $J_{C\text{-}1,H\text{-}1}$ 172.4 and $J_{C\text{-}4'H\text{-}4'}$ 147.7 Hz for **15**, and $J_{C\text{-}1,H\text{-}1}$ 170.3 for **16** in aqueous solution obtained by DEPT experiments. The magnitude of the calculated $<^1J_{C,H}>$ values for **16** and for the aglycon C–H bond in **15** are in excellent agreement with the experimental values. The discrepancy between the experimental and calculated $^1J_{C,H}$ values for the C-1–H-1 bond in **15** might indicate that the four conformers do not describe the conformational equilibrium quantitatively in aqueous solution. A smaller calculated $^1J_{C,H}$ value, in comparison with the experimental one, might suggest that the conformers with larger $^1J_{C,H}$, *i.e.*, Φ^{H} ~180°, should be present in the equilibrium. This conclusion is supported also by the difference between the calculated and the experimental values, found for aqueous solutions, for $^3J_{C,H}$ (ref. 10).

The spread of calculated ${}^1J_{C,H}$ values (Figs. 4 and 5) represents the influence of the orientation of aglycon (*i.e.*, the value of Ψ^H), which demonstrates the limits of a general application of the derived equations. Nevertheless, the results suggest that, for Ψ^H and Φ^H, the prediction of ${}^1J_{C,H}$ values from angles can be made with an accuracy of ± 1 Hz, and the reverse prediction with an accuracy of ± 10°. This accuracy is sufficient to use ${}^1J_{C,H}$ values to determine the conformations of carbohydrates in solution.

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