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^{13}C–^{13}C Spin–Spin Coupling Constants in Structural Studies: XXXV. Stereochemical Study of the Furanose Ring

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Abstract—Theoretical conformational analysis and calculation of ^{13}C–^{13}C spin–spin coupling constants of aldofuranoses of the D-series were performed in terms of the self-consistent finite perturbation theory in the INDO approximation. All the examined furanoses were found to prefer an *envelope* conformation. The main factor responsible for the stereospecificity of the $^{1}J_{1,2}$ coupling constant is mutual orientation of the hydroxy groups on C^1 and C^2: *s-trans* isomers are characterized by greater $^{1}J_{1,2}$ values (by 2–4 Hz) than the corresponding *s-cis* isomers.

Aqueous solutions of aldoses contain complex mixtures of species. It is known that the equilibrium mixture consists of at least six forms: two pyranoses, two furanoses, aldehyde isomer, and hydrate of the latter [1, 2]. Conformational behavior of five-membered furanose isomers of monosaccharides has been studied to a much lesser extent than the behavior of six-membered pyranose isomers. This is explained mainly by low stability and hence low concentration of furanose isomers. In addition, furanose rings in solution are characterized by high conformational lability which strongly complicates their study [3]. Nevertheless, solutions of almost all aldoses contain more or less significant amounts of furanose forms. Exceptions are D-glucose and D-mannose: the concentration of the corresponding furanose isomers is less than 1% [2]. It is often difficult to unambiguously assign configuration of the anomeric center in furanoses, metabolites derived therefrom, and other biological molecules having a furanose moiety, and conformational analysis of these species by conventional methods is not always possible.

Cloran *et al.* [4, 5] studied in detail conformations of the furanose ring and streochemical behavior of ^{13}C–^{1}H and ^{13}C–^{13}C coupling constants in 2-deoxy-β-D-ribofuranosylamide and 2-deoxy-β-D-erythrofuranose on the basis of quantum-chemical calculations in terms of the density functional theory (DFT). With the goal of elucidating new potentialities in stereochemical analysis of carbohydrates having furanose fragments, we calculated the direct ^{13}C–^{13}C coupling constants of the anomeric carbon atom in α- and β-anomers of all possible aldofuranose forms of D-monosaccharides: two tetrofuranoses, four pentofuranoses, and eight hexofuranoses. The calculations were performed in terms of the self-consistent finite perturbation theory (SCPT) in the INDO approximation.

Theoretically, two most stable conformations of the five-membered ring in furanoses are possible: *E* (*envelope*; four atoms of the ring lie in one plane) and *T* (*twist*; three atoms of the ring lie in one plane) [6]. The numbers of atoms located above or below that plane are indicated, respectively, as superscripts or subscripts before or next to the letter *E* or *T*, e.g., E_2 or $^{3}T_2$. We used such notations in this paper.

Like pyranoses, cyclic furanose molecules can exist as two anomers. When the configuration of the anomeric (semiacetal, C^1) center is the same as that of the asymmetric carbon atom determining affiliation to the D- or L-series (C^3 in tetrofuranoses, C^4 in pentofuranoses, and C^5 in hexofuranoses), the isomer is referred to as α-anomer. As shown in [7, 8], a furanose ring can adopt up to 10 symmetric *twist* (*T*) conformations, 10 *envelope* (*E*) conformations, and one planar form. It is well known that exocyclic bonds at the furanose ring approach in their orientation equatorial and axial bonds in pyranoses; therefore, they are called, respectively, quasiequatorial and quasiaxial. As well as in pyranoses, substituents in furanoses (except for anomeric ones) occupy quasiequatorial positions [3, 6], wheres the oxygen atom

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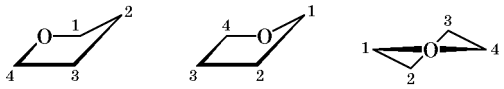
at the anomeric carbon atom is preferentially quasi-axial due to anomeric effect [9, 10].

According to the results of many authors, the most favorable furanose conformation is that with exo-planar arrangement of the C^2 atom of the furanose ring (E^2). An electron-acceptor substituent on C^1 in the ^2E conformation does not exert an appreciable anomeric effect, for dipole interactions of that substituent with the ring oxygen atom in both anomers are fairly similar. On the other hand, the same substituent in stable ^1E conformer induces a strong anomeric effect and is therefore oriented axially. The following is also important: the strongest interaction in furanose rings is 1,2-*cis*, while 1,3-*cis*-interaction is the strongest in pyranoses. A *twist* conformation of furanoses ($^3T_2$), in which the C^2 and C^3 atoms appear, respectively, below and above the plane formed by the remaining three atoms, is also among the most stable ones [10]. Three most favorable conformations of the furanose ring are shown below [3, 6]:



^2E ^1E $^3T_2$

Furanose rings constitute important fragments of nucleic acids, and they are responsible in many respects for the structure, conformations, and dynamics of these natural polymers. Intrinsic mobility of furanose rings, i.e., their ability to readily adopt *twist* or *envelope* conformation (through a relatively low activation barrier), is well studied. Interconversion between the above conformers may occur via pseudorotation [11] which does not involve planar form as transition state. On the other hand, any two conformers may be transformed into each other through planar form as a result of inversion of the five-membered ring.

The C^1 and ^1C conformations of six-membered pyranose rings are separated by a relatively high energy barrier and are well studied. By contrast, the energy difference between numerous *twist* and *envelope* conformers of five-membered furanoses is so small that their conformational analysis involves considerable experimental difficulties [12, 13].

Up to now, five intramolecular factors responsible for conformational behavior of furanoses have been revealed. These are: (a) anomeric effect [14, 15]; (b) preferential quasiequatorial orientation of side chains [16]; (c) variable orientation of substituents in the ring [17]; (d) so-called *gauche* effect [15]; and (e) preferentially tetrahedral bond angles between the endocyclic carbon–carbon bonds [18]. Only four of the above five factors apply to tetrofuranoses which, unlike pento- and hexofuranoses, contain no side chains.

Conformations and dynamics of furanose rings in oligo- and polynucleotides, enzymes, ribonucleic acids (RNA), and deoxyribonucleic acids (DNA) play an important role in the behavior of these macromolecules in solution. For example, the ability of DNAs to adopt various conformations is determined in part by the mobility of their furanose components. The energy aspects of conformational transformations of DNAs and RNAs can be understood only when the dynamics of conformational behavior of furanose ring is known.

NMR spectroscopy is widely used for determination of anomeric configuration and conformational analysis of biological molecules containing carbohydrate fragments [19]. An important parameter is ^{13}C–^{13}C coupling constants which are very sensitive to stereochemical effects [20, 21]. The available experimental data on ^{13}C–^{13}C coupling constants in cyclic forms of monosaccharides [4, 5, 22, 23] show that these constants depend on the conformation and anomeric configuration. Specific interest in ^{13}C–^{13}C coupling constants in carbohydrates gives rise to wide use in biochemical studies of their derivatives selectively labeled with ^{13}C isotope [19]. In this case, experimental measurement of ^{13}C–^{13}C coupling constants is a simple procedure: the constants can be determined from a routine ^{13}C NMR spectrum recorded with broad-band decoupling from protons.

In the present study we performed theoretical calculations of ^{13}C–^{13}C coupling constants in furanose ring with the goal of elucidating the nature of stereochemical relations and ways of their utilization in stereochemical analysis of biological species containing a furanose ring. Our interest in $^1J_{1,2}$ values (i.e., those involving the anomeric carbon atom) is explained by the fact that just the C^1–C^2 coupling constant is most sensitive to configuration and conformational behavior of hydrocarbons [20, 22, 23].

Before proceeding to the calculations, we focused on the determination of preferential conformations of the furanoses under study. For this purpose, two methods for optimization of geometric parameters were used: AM1 semiempirical method (NDDO group) and nonempirical restricted Hartree–Fock (RHF) method for closed shells with Pople's standard polarizational basis set 6-31G*. As follows from our previous data of nonempirical calculations, the use of

polarizational *p*-functions on hydrogen atoms in the 6-31G** basis set almost does not affect the results, as compared to 6-31G*, but the computation time considerably increases.

According to the results of AM1 and HF/6-31G* calculations, the preferential conformation of all the examined furanoses is *envelope*. In none of the cases, the most stable *twist* form $^3T_2$ [3, 6] was preferred. Conformations of the furanose ring were assigned to one or another *envelope* form on the basis of the dihedral angle φ between the triangle plane including the carbon or oxygen atom deviating from the main ring plane and the main ring plane itself (formed by the remaining four atoms). The angle φ was the maximal for *envelope* conformers. The complete data set is available from the authors.

In keeping with the HF/6-31G* data, all furanose forms of monosaccharides are considerably less planar (φ ≈ 30–40°) than those calculated by the AM1 method (φ ≈ 15–20°). The dihedral angles obtained in terms of different geometry optimization methods are also different. According to the results of nonempirical calculations, the most nonplanar structure (φ > 40°) is characteristic of α-D-allose (E_1), α-D-altrose (E_1), α-D-glucose (E_4), β-D-glucose (E_2), α-D-gulose (^2E), and β-D-galactose (^1E), while β-D-xylose (^4E) and β-D-lyxose (E_O) have the most planar structures (φ < 30°). In most cases, the preferential *envelope* conformer is ^2E; the same result was also obtained by other authors [6, 7]. This conformer is typical of the α-anomers of D-erythrose, D-ribose, D-xylose, D-lyxose, D-gulose, D-idose, and D-talose (AM1 and HF/6-31G*), as well as of α-D-allose (AM1) and α-D-galactose (HF/6-31G*). It should be noted that only the α-anomers of D-aldofuranoses adopt ^2E conformation.

Another most frequently encountered conformation of the furanose ring is ^4E. It is typical of β-D-lyxose and β-D-talose (AM1 and HF/6-31G*), β-D-erythrose (AM1), β-D-arabinose (AM1), β-D-gulose (AM1), β-D-idose (AM1), and β-D-xylose (HF/6-31G*). Characteristically, ^4E conformation was found only for the β-anomers of D-aldofuranoses. In addition, E_1 (α-D-threose, α-D-altrose, α-D-arabinose, β-D-arabinose, α-D-allose, β-D-allose, β-D-mannose, and α-D-galactose), E_O (β-D-threose, β-D-ribose, β-D-xylose, β-D-altrose, and β-D-idose), and E_3 conformers (β-D-erythrose, α-D-arabinose, β-D-allose, and β-D-gulose) were found.

Thus the preferential conformation of the furanose ring is ^2E (*envelope*). Also, ^4E, E_1, E_O, and E_3 conformers exist, the ^2E conformation being typical of only the α-anomers of the D-series, and ^4E and E_O, of the corresponding β-anomers.

Semiempirical calculation of ^{13}C–^{13}C coupling constants in organic molecules on the basis of empirical parameters which specify, in particular, *s*-electron density and *p*-orbital radius of carbon atoms is impossible without proper choice of the geometry optimization procedure. This is especially important for carbohydrates from the viewpoint of correct consideration of conformations originating from rotation of hydroxy groups about the C–O bonds [5] (this problem will be the subject of a separate communication). In the present work we compared conventional semiempirical methods for geometry optimization of the NDDO group (MNDO, AM1, PM3) and nonempirical methods in terms of both the SCF RHF theory for closed shells and density functional theory (DFT) with the most popular Becke three-parameter hybrid potential [24] in combination with the Lee–Yang–Parr correlation functional (B3LYP) [25], as well as in terms of the Moeller–Plesset second-order perturbation theory (MP2) with inactive ("frozen") inner-shell electrons. In the nonempirical calculations we used standard Pople's polarizational basis sets 6-31G* and 6-31G** [26] and also triply split polarizational basis set 6-311G** [27] optimized for nonempirical calculations with account taken of electronic correlation.

The results showed that in most cases nonempirical calculations give fairly similar geometric parameters and that consideration of electronic correlation at the DFT or MP2 level has no appreciable effect on the bond lengths and bond and dihedral angles. Among semiempirical methods, the results of AM1 calculations approach most closely those of nonempirical methods, while the results of MNDO calculations differ most strongly. In particular, the latter method clearly overestimates the C^1–C^2 bond length, which is crucial in the calculations of ^{13}C–^{13}C coupling constants. As concerns $^1J_{1,2}$ values calculated on the basis of geometric parameters optimized by different methods, MP2/6-31G** gives a $^1J_{1,2}$ value of 43.0 Hz for α-D-erythrose, which is very close to the experimental value (43.2 Hz), whereas $^1J_{1,2}$ = 48.0 Hz for β-D-erythrose (experimental value 46.8 Hz) was obtained by the HF/6-311G** method. On the whole, nonempirical geometry optimization methods give rise to $^1J_{1,2}$ values which are more consistent with the experimental data. Among semiempirical methods, the AM1 procedure ensures best reproduction of the experimental ^{13}C–^{13}C coupling constants. The complete set of the calculation results is available from the authors.

Table 1. ^{13}C–^{13}C Coupling constants (Hz) in aldofuranoses, calculated by the SCPT INDO method

Compound	Mutual orientation of C^1-OH and C^2-OH	J_{SO}	J_{SD}	J_{FC}	$^1J_{1,2}$[a]
D-Erythrose:					
α-D-Ery-^2E (**Ia**)	*s-cis*	–2.2	1.4	46.2	45.3 (43.2)
β-D-Ery-^4E (**Ib**)	*s-trans*	–2.3	1.4	50.6	49.7 (46.8)
D-Threose:					
α-D-Thre-E_1 (^2E)[b] (**IIa**)	*s-trans*	–2.4	1.4	50.2	49.2 (46.1)
β-D-Thre-E_O (**IIb**)	*s-cis*	–2.3	1.4	46.5	45.5 (42.5)
D-Arabinose:					
α-D-Ara-E_3 (**IIIa**)	*s-trans*	–2.3	1.4	50.1	49.1
β-D-Ara-^4E (**IIIb**)	*s-cis*	–2.3	1.3	49.1	48.1
D-Ribose:					
α-D-Rib-^2E (**IVa**)	*s-cis*	–2.2	1.4	46.2	45.3 (42.6)
β-D-Rib-E_O (**IVb**)	*s-trans*	–2.4	1.4	48.0	47.0 (46.1)
D-Xylose:					
α-D-Xyl-^2E (**Va**)	*s-cis*	–2.3	1.3	46.5	45.5
β-D-Xyl-E_O (**Vb**)	*s-trans*	–2.3	1.4	50.3	49.4
D-Lyxose:					
α-D-Lyx-^2E (E_3) (**VIa**)	*s-trans*	–2.4	1.4	47.3	46.3
β-D-Lyx-^4E (**VIb**)	*s-cis*	–2.3	1.3	48.7	47.7
D-Allose:					
α-D-All-^2E (**VIIa**)	*s-cis*	–2.2	1.4	46.2	45.3
β-D-All-E_3 (**VIIb**)	*s-trans*	–2.3	1.4	50.3	49.3
D-Altrose:					
α-D-Alt-E_1 (**VIIIa**)	*s-trans*	–2.4	1.4	47.5	46.5 (46.3)
β-D-Alt-E_O (^1E) (**VIIIb**)	*s-cis*	–2.3	1.3	46.3	45.2 (48.8)
D-Glucose:					
α-D-Glu-^OE (**IXa**)	*s-cis*	–2.3	1.3	46.9	45.9
β-D-Glu-^3E (**IXb**)	*s-trans*	–2.4	1.4	50.2	49.3
D-Mannose:					
α-D-Man-E_4 (**Xa**)	*s-trans*	–2.3	1.4	48.2	47.3
β-D-Man-^OE (**Xb**)	*s-cis*	–2.3	1.3	47.1	46.1
D-Gulose:					
α-D-Gul-^2E (**XIa**)	*s-cis*	–2.2	1.4	46.4	45.5
β-D-Gul-^4E (**XIb**)	*s-trans*	–2.4	1.4	48.4	47.4
D-Idose:					
α-D-Ido-^2E (**XIIa**)	*s-trans*	–2.4	1.4	47.2	46.2 (45.2)
β-D-Ido-E_O (^4E) (**XIIb**)	*s-cis*	–2.3	1.3	47.0	46.0 (42.3)
D-Galactose:					
α-D-Gal-E_1 (**XIIIa**)	*s-cis*	–2.3	1.3	46.7	45.7
β-D-Gal-^1E (**XIIIb**)	*s-trans*	–2.4	1.4	47.8	46.8
D-Talose:					
α-D-Tal-^2E (**XIVa**)	*s-trans*	–2.4	1.4	47.6	46.6 (46.1)
β-D-Tal-^4E (**XIVb**)	*s-cis*	–2.3	1.3	47.5	46.4 (42.3)

[a] In parentheses are given the experimental values [24].
[b] Alternative assignment is possible.

Naturally, while choosing a procedure for geometry optimization, we were interested in proper reproduction of experimental $^{13}C–^{13}C$ coupling constants, but more important was reproduction of stereochemical effects in $^1J_{1,2}$ values (i.e., differences in $^1J_{1,2}$ for α- and β-anomers of the furanoses under study, for which experimental $^{13}C–^{13}C$ coupling constants are known). Moreover, taking into account a great deal of computation, we tried to choose an optimal geometry optimization procedure from the viewpoint of saving computation time. For example, optimization of the geometric parameters of only α-D-erythrose by the B3LYP/6-311G** method took 2 days!).

Stereochemical effects (here, the observed difference in the experimental $^1J_{1,2}$ values for α- and β-anomers of D-erythrose) are well reproduced by all geometry optimization methods. However, taking into consideration saving of computation time, in the calculation of $^{13}C–^{13}C$ coupling constants in the series of compounds **Ia**–**XIVb** we used geometric parameters, optimized by the AM1 semiempirical method.

In the present work we calculated by the SCPT INDO method [28] the $^{13}C–^{13}C$ coupling constants between C^1 and C^2 atoms ($^1J_{1,2}$) in the α- and β-anomers of two aldotetrofuranoses (erythrose and threose), four aldopentofuranoses (arabinose, ribose, xylose, and lyxose), and eight aldohexofuranoses (allose, altrose, glucose, mannose, gulose, idose, galactose, and talose), i.e., for all possible forms of tetro-, pento-, and hexofuranoses. The calculated total $^1J_{1,2}$ values and contributions thereto (Fermi-contact J_{FC}, spin–dipole J_{SD}, and spin–orbital J_{SO}) are given in Table 1. Depending on the steric structure of the furanose ring, the range of variation of the calculated $^1J_{1,2}$ values exceeds 4 Hz. It is seen that the calculated values are very consistent with the available experimental data. In all cases, the Fermi-contact contribution prevails. The spin–orbital constituent is negative, and it changes within a very narrow range, from –2.4 to –2.2 Hz, while the positive spin–dipole contribution is almost constant (1.3–1.4 Hz). Thus the overall contribution of noncontact interactions (which are characterized by opposite signs) is negligible, and it almost does not depend on the configuration and conformation of the furanose ring. Therefore, just the Fermi-contact contribution is responsible for sensitivity of $^{13}C–^{13}C$ coupling constants to stereochemical effects in the furanose ring. This conclusion is important, for nonempirical calculations of $^{13}C–^{13}C$ coupling constants in carbohydrates can thus be reduced to determination of only Fermi-contact contribution, which requires much less computation time (by an order of magnitude) than the calculation of spin–dipole contribution. Serianni and co-workers [4, 5, 29] recently performed for the first time such calculations of carbohydrates in terms of the density functional theory (DFT/B3LYP).

The main factor responsible for stereochemical behavior of $^{13}C–^{13}C$ coupling constants in the furanose ring is mutual orientation of the hydroxy groups on C^1 and C^2. It is seen that $^1J_{1,2}$ values for *s-trans* isomers are greater on the average by 2–4 Hz than those found for the corresponding *s-cis* isomers. This relation is clearly observed for all aldofuranoses (as well as for the available experimental data), except for α- and β-anomers of idose (**XIIa**, **XIIb**) and talose (**XIVa**, **XIVb**), for which the difference is insignificant (0.1–0.2 Hz). It should be kept in mind that furanose anomers are capable of adopting various conformations, which complicates interpretation of the obtained data. Nevertheless, mutual orientation of the hydroxy group is the main factor determining stereospecificity of $^1J_{1,2}$, regardless of the furanose ring conformation.

Taking into account importance of our results for stereochemical analysis of carbohydrates having a furanose fragment, we made an attempt to understand the nature of the observed relations in terms of the CLOPPA approach [30] which analyzes contributions of particular localized molecular orbitals (LMO) to the total $^1J_{1,2}$ value in the INDO approximation. At this level, the $^{13}C–^{13}C$ coupling constants calculated by the CLOPPA and SCPT methods are similar. Therefore, we can compare the results of SCPT and CLOPPA calculations.

In keeping with the CLOPPA approach, which is based on the polarizational propagator theory [31], each coupling constant $^1J_{1,2}$ is divided into a large number of elementary contributions originating from two-species excitation involving two occupied and two vacant LMOs. The latter may correspond to lone electron pairs on oxygen atoms and C–C, C–O, C–H, and O–H bonds of the pyranose fragment. These contributions are calculated via localization of initial MOs. Table 2 gives the most interesting (in our opinion) LMO contributions to $^1J_{1,2}$ for anomers of D-erythrose and D-threose, which are most sensitive to the stereochemical effects under discussion. It is seen that the largest contribution to $^1J_{1,2}$ is that of the $C^1–C^2$ bond: it ranges from 52.2 to 57.7 Hz. Next follow contributions of the $C^2–C^3$ and $C^2–H$ bonds (1.7 to 2.5 Hz), while those of $C^1–O^1$, $C^2–O^2$, $C^1–O^5$, and $C^1–H$ are insignificant (less than 1 Hz). The overall contributions from two LEPs of the oxygen atoms (O^1, O^2, and O^5), as well as contributions of both O–H bonds at C^1 and C^2, are negligible.

Table 2. Contributions (Hz) of localized molecular orbitals (LMO) to ^{13}C–^{13}C coupling constants $^1J_{1,2}$ of α- and β-anomers of erythrose and threose, calculated by the CLOPPA INDO method

LMO	α-D-Ery-^2E (**Ia**)	β-D-Ery-^4E (**Ib**)	α-D-Thre-^2E (E^1) (**IIa**)	β-D-Thre-E_O (**IIb**)
C^1-C^2	52.2	57.7	57.1	53.5
C^1-H	0.4	0.5	0.6	0.1
C^1-O^1	0.0	0.2	0.2	0.1
C^1-O^5	0.7	0.8	0.8	0.8
C^2-H	1.8	2.4	2.2	1.7
C^2-O^2	0.0	0.1	0.1	0.0
C^2-C^3	2.5	2.2	2.3	2.4
O^1-H	0.0	0.0	0.0	0.0
LEP(O^1)[a]	0.0	0.0	0.0	0.0
LEP(O^5)[a]	0.0	0.0	0.0	0.0
O^2-H	0.0	0.0	0.0	0.0
LEP(O^2)[a]	0.0	0.0	0.0	0.0
Overall contribution	57.6	63.9	63.3	58.6
Experimental value[b]	45.3	49.7	49.2	45.5

[a] Overall contribution of two lone electron pairs.
[b] Data of [24].

This result was quite surprising. On the basis of the results of our studies on the effect of oxygen LEP on $^1J_{CC}$ in alcohols [32] and ethers [33], we believed that just the contributions of oxygen LEP and O–H bonds at the C^1 and C^2 are responsible for the observed differences between the coupling constants. Nevertheless, we tried to analyze the contributions of molecular fragments (chemical bonds and lone electron pairs), which could explain stereochemical effects on $^1J_{1,2}$ for different anomers and conformers.

As follows from the data in Table 2, the difference in $^1J_{1,2}$ values for α- and β-anomers of the examined furanoses results mainly from LMO contributions of the C^1-C^2 and C^2-H bonds, i.e., bonds involving the C^2 atom. For example, the different $^1J_{1,2}$ values of the D-erythrose anomers may be interpreted in terms of the greater contribution of the C^1-C^2 LMO (by 5.5 Hz) and smaller contribution of the C^2-H LMO (by 0.6 Hz) in the α-anomer. The same contributions are responsible for the observed difference in $^1J_{1,2}$ for the α- and β-anomers of D-threose.

Summarizing the results presented in Tables 1 and 2, it should be noted that the observed variations in $^1J_{1,2}$ for different anomers and conformations of the furanose ring are quantitatively reproduced by the SCPT INDO calculations. Analysis of the LMO contributions in terms of the CLOPPA INDO method shows that the main contributions responsible for the observed differences are those of the C^1-C^2 and C^2-H bonds and that the contributions of the other bonds and LEPs on the oxygen atoms are insignificant (the latter turned out to be quite surprising).

Thus the results of our calculations indicate that direct coupling constants between the C^1 and C^2 nuclei in furanose forms of monosaccharides are very sensitive, on the one hand, to orientation of the anomeric hydroxy group and, on the other, to conformation of the furanose ring in cases when different conformers are characterized by different mutual orientations of the hydroxy groups on C^1 and C^2.

EXPERIMENTAL

Quantum-chemical calculations were performed with the use of SCPTINDO, CLOPPA, MOPAC [34], GAMESS [35], and DALTON [36] software operating under Linux Red Hat 7.2 (Kernel 2.4.7-10) on a PC Pentium 4 (1400 MHz, RAM 1536 Mb, HDD 70 Gb). In the SCPT INDO calculations of ^{13}C–^{13}C coupling constants, the following parameters for carbon atoms were used: *s*-electron density on the nucleus $s^2_{C(0)}$ = 3.2328; reciprocal of the cubed 2*p*-orbital radius $\langle r^{-3}\rangle$ = 2.8256.

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