*Russian Journal of Organic Chemistry, Vol. 40, No. 1, 2004, pp. 57–62. Translated from Zhurnal Organicheskoi Khimii, Vol. 40, No. 1, 2004, pp. 66–71.*


# $^{13}C–^{13}C$ Spin–Spin Coupling Constants in Structural Studies: XXXVI. Stereochemical Study of the Septanose Ring

**V. A. Danilova and L. B. Krivdin**

*Angarsk State Technical Academy, ul. Chaikovskogo 60, Angarsk, 665835 Russia*
*e-mail: krivdin@irk. ru*

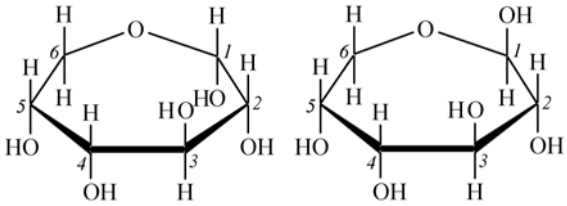
Received October 11, 2002

**Abstract**—$^{13}C–^{13}C$ Spin-spin coupling constants of aldoseptanoses of the *D* series were calculated in terms of the self-consistent finite perturbation theory. General relations holding in the stereochemical behavior of the $^{13}C–^{13}C$ coupling constants in the septanose ring were determined, which made it possible to perform conformational analysis and assign configuration of the anomeric centers in carbohydrates and products of their metabolism.

NMR spectroscopy is widely used for determination of configuration of the anomeric center in biological molecules containing carbohydrate fragments [1]. Important NMR parameters are spin–spin coupling constants with carbon nuclei which are sensitive to stereochemical effects depending on the molecular conformation [2–5]. Specific interest in $^{13}C–^{13}C$ coupling constants in carbohydrates arises from the wide application in biochemical studies of carbohydrate derivatives selectively labeled with $^{13}C$ isotope [1], where experimental measurement of $^{13}C–^{13}C$ coupling constants is a routine procedure: they can be determined directly from standard $^{13}C$ NMR spectrum recorded with broad-band decoupling from protons.

The goal of the present study was to calculate $^{13}C–^{13}C$ coupling constants in septanose ring with a view to reveal stereochemical relations, examine their nature, and elucidate prospects in their use in stereochemical analysis of biological molecules having a septanose ring. Our interest in the direct $^{13}C–^{13}C$ coupling constants $^{1}J_{1,2}$ 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 cyclic carbohydrates [2, 4, 5].

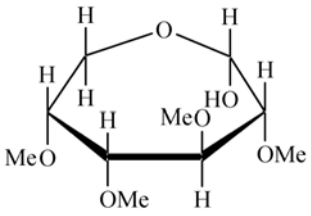
Aqueous solutions of aldoses contain complex mixtures of species. It is known that the equilibrium mixture consists of at least six forms: two pyranoses, two furanoses, aldehyde isomer, and hydrate of the latter [6]. Apart from the above, one more exotic cyclic isomer could exist, namely septanose. Like pyranoses and furanoses, septanose forms of each monosaccharide differ by the configuration of the anomeric center, as shown below:



α-D-Glucoseptanose β-D-Glucoseptanose

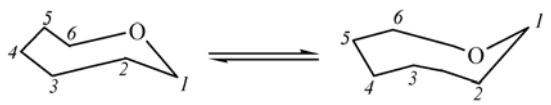
Thus cyclic septanose species can exist as two anomers: in α-anomer, the configuration of the anomeric center (semiacetal $C^1$ carbon atom) coincides with that of the $C^5$ atom which determines whether the carbohydrate molecule belongs to the D- or L-series.

It is known [7] that the most stable tautomeric form of monosaccharides is six-membered pyranose ring which adopts a normal or alternative *chair* conformation. Five-membered furanose rings are as a rule less stable; nevertheless, almost all aldoses in solution give rise to an appreciable amount of equilibrium furanose isomers which could be detected by various physical methods, including $^{13}C$ NMR spectroscopy [8]. Cyclic septanose isomers are very unstable. Such structures were isolated only for D-idose. According to the $^{13}C$ NMR data, an equilibrium aqueous solution of D-idose at 37°C contains 1.6% septanose anomers [9]. On the other hand, some septanose derivatives were successfully synthesized, and they turned out to be fairly stable [10]. The results of studying a solution of 2,3,4,5-tetra-*O*-methylglucose were very interesting. The structure of this compound permits formation of neither six- nor five-membered ring. Therefore, it exists in solution as a mixture of acyclic and septanose form [11]; the α-anomer of the latter is shown below:




We can conclude that the stability (or, more exactly, instability) of septanose isomers approaches that of aldehyde forms and that they are considerably less stable than other cyclic monosaccharide species, furanoses and pyranoses. Nevertheless, despite exotic character and low stability, septanose forms of saccharides and products of their metabolism or microbiological transformations are quite real subjects for stereochemical analysis of configuration and conformational behavior.

In order to estimate the possibility of using direct $^{13}C$–$^{13}C$ coupling constants with the anomeric carbon atom for stereochemical analysis of carbohydrates having septanose fragments, we calculated their values in terms of the self-consistent finite perturbation theory (SCPT INDO [12]) for the α- and β-anomers of all possible (eight) aldoseptanose forms of D-monosaccharides by analogy with the two preceding studies, where such calculations were performed for pyranose [13] and furanose [14] isomers. Septanoses are assigned to the α- or β-series according to the configuration of the anomeric center, i.e., orientation of the anomeric hydroxy group. Determination of the conformation of septanose ring is a much more difficult problem which sometimes cannot be solved unambiguously. First information on the conformations of seven-membered forms of monosaccharides appeared only in 1970s [9, 11]. In particular, preferential *chair*-like conformation of the septanose ring was presumed on the basis of the X-ray diffraction and NMR data. Taking into account the results of these studies, we proceeded from the fact that, by analogy with pyranoses, each anomer of the examined septanoses exists as an equilibrium mixture of normal (C1) and alternative (1C) *chair* conformation, as shown below:




Normal conformation C1 Alternative conformation 1C.

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 in pyranose and furanose rings about the C–O bonds [15] (this problem will be the subject of a separate communication within the given series). 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 [16] in combination with the Lee–Yang–Parr correlation functional (B3LYP) [17]. In the nonempirical calculations we used standard Pople's polarizational basis sets 6-31G** [18] (including *p* functions on hydrogen atoms and *d* functions on carbon and oxygen atoms), triply split polarizational basis set 6-311G** [19] (optimized with account taken of electronic correlation), and Dunning's standard correlation-consistent basis set cc-p-VDZ [20] (which was also optimized for calculations with account taken of electronic correlaton).

While selecting a procedure for optimization of geometric parameters, we were interested primarily in revealing stereochemical effects on $^1J_{1,2}$ values (i.e., different $^1J_{1,2}$ values for α- and β-anomers, as well as for different conformations of the same anomer), as was observed in the case of pyranoses and furanoses [4, 5, 13, 14]. 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 one form of α-D-mannoseptanose C1 by the B3LYP/cc-pVDZ method took more than 11 days). For this purpose, we compared $^1J_{1,2}$ values calculated by the SCPT INDO method for the normal conformation (C1) of both mannose anomers whose geometric parameters were optimized by different procedures. The results showed that, among three semiempirical methods (MNDO, AM1, and PM3), only the geometric parameters optimized by the AM1 procedure give rise to $^{13}C$–$^{13}C$ values which agree well with those calculated by nonempirical methods. Therefore, in the subsequent study we used the AM1 method for geometry optimization of the whole septanose series.

The calculated $^{13}C$–$^{13}C$ coupling constants $^1J_{1,2}$ for each conformer (C1 and C2) of α- and β- anomers of eight aldoseptanoses are collected in Table 1. Unfortunate-ly, up to now no experimental $^1J_{1,2}$value for septanose ring has been reported. Therefore, the calculated data can be compared only with the experimental data for the

corresponding pyranoses [5] which may be regarded as most related septanose models. In fact, we observed a good quantitative agreement between the calculated $^1J_{1,2}$ values for septanoses and the experimental $C^1$–$C^2$ coupling constants for the respective pyranoses. The calculated $^1J_{1,2}$value for α-D-alloseptanose C1 (45.4 Hz) coincided with that found experimentally for α-D-allopyranose. A good agreement with the corresponding experimental coupling constants of pyranoses was also found for β-D-galactose C1, β-D-gulose C1, α-D-altrose C1, β-D-allose C1, β-D-mannose C1, and α-D-idose C1: the difference between the calculated and experimental coupling constants was as small as 0.1–0.5 Hz. In the only case, this difference was appreciable, ~2 Hz for β-D-idose C1.

In keeping with the Ramsey fundamental non-relativistic perturbation theory of spin–spin interactions [21], a total spin–spin coupling constant includes three different contributions arising from three different and physically inseparable mechanisms of nuclear magnetic spin interactions thorugh bond electrons (indirect spin–spin interaction): Fermi-contact (FC), i.e., a contact interaction between nuclear and electron spins directly over the surface of the nucleus; spin–dipole (SD), i.e., a dipole interaction between spatially distant nuclear and electron spins; and spin–orbital (SO), i.e., interaction between nuclear spin and orbital angular moments of electrons (here, we do not divide spin–orbital interactions into diamagnetic and paramagnetic constituents). Therefore, the total coupling constant may be represented as the sum of three contributions:

$$J = J_{FC} + J_{SD} + J_{SO}.$$

As follows from the data in Table 1, the Fermi-contact contribution always predominates. The spin-orbital contributions in the examined monosaccharide series is negative, and it changes within a very narrow range, while the positive spin-dipole contribution to $^1J_{1,2}$ for all compounds remains almost constant. The sum of the two latter (noncontact) contributions which have opposite signs is negligible, and it does not depend on the conformation and configuration of the septanose ring. Thus just the Fermi-contact contribution is responsible for stereospecificity of the $^{13}C$–$^{13}C$ coupling constants. This conclusion is very important, for nonempirical calculations of $^{13}C$–$^{13}C$ coupling constants in carbohydrates require a lot of time. The calculation of only Fermi-contact contribution is by an order of magnitude more economic (from the viewpoint of computational time) than analogous calculation of the spin-dipole contribution.

**Table 1.** $^{13}C$–$^{13}C$ Coupling constants (Hz) between the $C^1$ and $C^2$ atoms in hexoseptanoses, calculated by the SCPT INDO method

| Compound | Orientation of the 1- and 2-OH groups | $J_{SO}$ | $J_{SD}$ | $J_{FC}$ | $^1J_{1,2}$ |
|---|---|---|---|---|---|
| D-Allose | | | | | |
| α–D-All-Cl (**Ia**) | *ae* | –2.1 | 1.4 | 46.2 | 45.4 |
| α–D-All-lC(**Ia**) | *ea* | –2.2 | 1.4 | 45.1 | 44.3 |
| (3-D-A11-Cl (**Ib**) | *ee* | –2.1 | 1.4 | 48.4 | 47.8 |
| β –D-A11-1C(**Ib**) | *aa* | –2.2 | 1.4 | 47.7 | 46.9 |
| D-Altrose | | | | | |
| α–D-Alt-Cl (**IIa**) | *aa* | –2.2 | 1.4 | 47.3 | 46.5 |
| α–D-Alt-lC (**IIa**) | *ee* | –2.1 | 1.4 | 46.4 | 45.8 |
| β –D-Alt-Cl (**IIb**) | *ea* | –2.2 | 1.4 | 46.2 | 45.4 |
| (3-D-Alt-lC (**IIb**) | *ae* | –2.1 | 1.4 | 47.3 | 46.6 |
| D-Glucose | | | | | |
| α-D-Glc-Cl (**IIIa**) | *ae* | –2.1 | 1.4 | 45.2 | 44.5 |
| α-D-Glc-lC(**IIIa**) | *ea* | –2.3 | 1.4 | 46.5 | 45.6 |
| (3-D-Glc-Cl (**IIIb**) | *ee* | –2.1 | 1.4 | 45.8 | 45.1 |
| (3-D-Glc-1C(**IIIb**) | *aa* | –2.2 | 1.3 | 49.9 | 49.1 |
| D-Mannose | | | | | |
| α-D-Man-Cl (**IVa**) | *aa* | –2.2 | 1.4 | 47.0 | 46.1 |
| α-D-Man-IC(**IVa**) | *ee* | –2.1 | 1.4 | 47.6 | 46.9 |
| (3-D-Man-Cl (**IVb**) | *ea* | –2.2 | 1.4 | 45.0 | 44.2 |
| β-D-Man-lC(**IVb**) | *ae* | –2.1 | 1.4 | 49.8 | 49.0 |
| D-Gulose | | | | | |
| α-D-Gul-Cl (**Va**) | *ae* | –2.1 | 1.4 | 45.9 | 45.1 |
| α-D-Gul-lC(**Va**) | *ea* | –2.2 | 1.4 | 45.3 | 44.5 |
| β-D-Gul-Cl (**Vb**) | *ee* | –2.1 | 1.4 | 48.2 | 47.5 |
| β-D-Gul-1C(**Vb**) | *aa* | –2.2 | 1.4 | 47.9 | 47.1 |
| D-Idose | | | | | |
| α-D-Ido-Cl (**Via**) | *aa* | –2.2 | 1.3 | 47.6 | 46.7 |
| α-D-Ido-IC(**Via**) | *ee* | –2.1 | 1.4 | 46.2 | 45.6 |
| β-D-Ido-Cl (**VIb**) | *ea* | –2.2 | 1.4 | 46.7 | 45.8 |
| β-D-Ido-lC(**VIb**) | *ae* | –2.1 | 1.4 | 46.8 | 46.1 |
| D-Galactose | | | | | |
| α-D-Gal-Cl (**VIIa**) | *ae* | –2.1 | 1.4 | 44.8 | 44.1 |
| α-D-Gal-lC(**VIIa**) | *ea* | –2.2 | 1.4 | 46.8 | 46.0 |
| β-D-Gal-Cl (**VIIb**) | *ee* | –2.1 | 1.4 | 46.7 | 46.0 |
| β-D-Gal-1C(**VIIb**) | *aa* | –2.2 | 1.3 | 47.3 | 46.4 |
| D-Talose | | | | | |
| α-D-Tal-Cl (**VIIIa**) | *aa* | –2.2 | 1.3 | 47.9 | 47.0 |
| α-D-Tal-lC (**VIIIa**) | *ee* | –2.1 | 1.4 | 47.4 | 46.8 |
| β-D-Tal-Cl (**VIIIb**) | *ea* | –2.2 | 1.4 | 45.0 | 44.1 |
| β-D-Tal-lC (**VIIIb**) | *ae* | –2.1 | 1.4 | 49.1 | 48.3 |

**Table 2.** Contributions of localized molecular orbitals (Hz) to the $^{13}C–^{13}C$ coupling constants of β-D-mannose $C^1$, calculated by the CLOPPA INDO method

| LMO | α-D-Man-C1 (**IVa**) | β-D-Man-C1 (**IVb**) |
|---|---|---|
| $C^1–C^2$ | 52.5 | 51.5 |
| $C^1$–H | 1.6 | –0.1 |
| $C^1–O^1$ | 0.4 | 0.1 |
| $C^1–O^5$ | 0.8 | 0.3 |
| $C^2$–H | 2.5 | 2.5 |
| $C^2–O^2$ | 0.0 | 0.0 |
| $C^2–C^3$ | 2.3 | 1.7 |
| $O^1$–H | 0.0 | 0.0 |
| LEP($O^1$) | 0.0 | 0.0 |
| LEP($O^5$) | 0.0 | 0.0 |
| $O^2$–H | 0.0 | 0.0 |
| LEP($O^2$) | 0.0 | 0.0 |
| Overall contribution | 60.1 | 56.0 |

Detailed analysis of the main stereochemical relations in variation of $^1J_{1,2}$ (Table 1) revealed the following:

(1) Normal conformations of hexoseptanoses with axial hydroxy group on $C^2$ are characterized by greater $^1J_{1,2}$ values (by about ~2 Hz) for the α-anomers relative to the β-anomers. In the first case, the hydroxy groups on $C^1$ and $C^2$ are axial, i.e., they are arranged *trans* with respect to each other. The anomeric hydroxy group in the β-anomers is equatorial. This relation is seen most clearly for normal conformers of altrose, mannose, idose, and talose. The observed difference in the coupling constant is quite sufficient for unambiguous assignment of configuration at the anomeric center in septanose ring;

(2) By contrast, normal conformations of septanoses with equatorial hydroxy group on $C^2$ are characterized by greater $^1J_{1,2}$ values for the β-anomers where the hydroxy group on $C^1$ is also equatorial, so that these hydroxy groups are arranged *gauche* with respect to each other. This relation is weakly expressed for the glucose anomers (the difference in the coupling constants is less than 1 Hz) but is clearly seen for allose, gulose, and galactose ($\Delta J \approx 2$ Hz);

(3) The coupling constants $^1J_{1,2}$ in alternative conformers of septanoses with axial and equatorial hydroxy group on $C^2$ are, on the average, by 1–3 Hz greater for the β-anomers with axial orientation of the anomeric hydroxy group than for the α-anomers in which the anomeric hydroxy group is equatorial. This relation is typical of alternative confomers of all the examined septanoses.

(4) In the β-anomers of septanoses with differently oriented hydroxy groups on $C^1$ and $C^2$ (i.e., with equatorial anomeric hydroxy group and axial hydroxy group on $C^2$ in the normal conformation or with axial anomeric hydroxy group and equatorial hydroxy group on $C^2$ in the alternative conformation), $^1J_{1,2}$ values for the normal conformers are smaller by 1–5 Hz than those found for the alternative conformers. This relation is most pronounced for β-D-altrose, β-D-mannose, β-D-idose, and β-D-talose.

Unlike the respective pyranoses [13], the coupling constants $^1J_{1,2}$ in the alternative septanose conformers with both axial and equatorial hydroxy group on $C^2$ are greater for the β-anomers as compared to α-anomers. Moreover, the α-anomers of pyranoses with differently oriented 1-OH and 2-OH groups are characterized by greater $^1J_{1,2}$ values for the normal conformers ($C^1$) than for alternative (1C) [13], whereas this relation is not observed for the α-anomers of septanoses. For example, $^1J_{1,2}$ values in the α-anomers of glucose and galactose with different orientations of the hydroxy groups on $C^1$ and $C^2$ are greater by 1–2 Hz for the alternative conformers (1C) as compared to normal.

It is seen that $^{13}C–^{13}C$ coupling constants in carbohydrates are clearly stereospecific, i.e., they are sensitive, on the one hand, to orientation of the anomeric hydroxy group in molecules existing in the same conformation and, on the other, to conformational structure of the same anomer. The above four relations may be regarded as a practical guide to assignment of anomeric configuration and conformational analysis of the septanose ring in carbohydrates. They can be reduced to two more general rules which relate $^{13}C–^{13}C$ coupling constants to orientation of the hydroxy groups on $C^1$ and $C^2$:

1. Carbohydrates with axial hydroxy groups on $C^1$ and $C^2$ (*aa*) are characterized by much greater $^1J_{1,2}$ values than the other anomers having equatorial anomeric hydroxy group and axial hydroxy group on $C^2$ (*ea*);

2. Carbohydrates with axial anomeric hydroxy group and equatorial hydroxy group on $C^2$ (*ae*) have as a rule larger coupling constant $^1J_{1,2}$ than their conformers with equatorial anomeric hydroxy group and axial hydroxy group on $C^2$ (*ea*).

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 [22] 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 [23], 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 septanose 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-mannose C1, 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. Next follow contributions of the $C^2$–H and $C^2$–$C^3$ bonds, while those of the $C^1$–$O^1$, $C^1$–$O^5$, and $C^1$–H bonds, as well as the overall contributions from two LEPs of the oxygen atoms and contributions of both O–H bonds at $C^1$ and $C^2$, are insignificant. 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 of septanoses.

As follows from the data in Table 2, the difference in $^1J_{1,2}$ values for the α- and β-anomers of D-mannose C1 results mainly from LMO contributions of the $C^1$–$C^2$ and $C^1$–H bonds, i.e., bonds involving the anomeric $C^1$ atom. For example, the difference in $^1J_{1,2}$ for anomers of mannose $C^1$ may be interpreted in terms of the larger contributions of the $C^1$–$C^2$ and $C^1$–H LMOs in the α-anomer than in the β-anomer (by 1 and 1.7 Hz, respectively).

Thus, the results of our calculations indicate pronounced stereospecificity of the $C^1$–$C^2$ coupling constants in septanose forms of monosaccharides, which is related to configuration of the anomeric center and conformation of the septanose ring.

The calculations were performed using SCPT INDO [12], CLOPPA [22], MOPAC [24], and GAMESS [25] programs operating under Linux Red Hat 7.2 (Kernel 2.4.7–10). In the calculations of $^{13}C$–$^{13}C$ coupling constants by the SCPT INDO method, the following parameters for the carbon atom were used: *s*-electron density on the nucleus $s^2C(0) = 3.2328$; 2*p*-orbital radius $\langle r^{-3} \rangle = 2.8256$.

This study was financially supported by the Russian Foundation for Basic Research (project no. 98-03-32882). The authors are grateful to G.E. Sal'nikov (Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences) for kindly providing latest versions of quantum-chemical programs.

## REFERENCES

1. Serianni, A.S., *$^{13}C$ Nuclear Magnetic Resonance Spectra of the Monosaccharides: Natural and Stable Isotopically Enriched Compounds*, NewYork: Omicron Biochemicals, 1986; Finley, J.W., Schmidt, S.J., and Serianni, A.S., *NMR Applications in Biopolymers*, New York: Plenum, 1990; Serianni, A.S., *Glycoconjugates: Composition, Structure, and Function*, Allen, H.J. and Kisailus, E.C., Eds., New York: Marcel Dekker, 1992, p. 71; Serianni, A.S., *NMR of Biological Macromolecules*, Stassinopoulou, C.I., Ed., New York: Springer, 1994, NATO ASI Series H: Cell Biology, vol. 87, p. 293.
2. Krivdin, L.B. and Kalabin, G.A., *Progress in NMR Spectroscopy,* Emsley, J.W., Feeney, J., and Sutcliffe, L.H., Eds., Oxford: Pergamon, 1989, vol. 21, p. 293.
3. Marshall, J. L. , *Carbon-Carbon and Carbon-Proton NMR Couplings: Applications to Organic Stereochemistry and Conformational Analysis,* Marchand, A.P., Ed., Deerfield Beach: Chemie, 1983; Krivdin, L.B. and Zinchenko, S.V., *Current Organic Chemistry,* Rahman, A., Ed., The Netherlands: Bentham Sci., 1998, vol. 2, p. 173; Krivdin, L.B. and Della, E.W., *Progress in NMR Spectroscopy,* Emsley, J.W., Feeney, J., and Sutcliffe, L.H., Eds., Oxford: Pergamon, 1991, vol. 23, p. 301.
4. Wu, J., Bondo, P.B., Vuorinen, T., and Serianni,A.S., *J. Am. Chem. Soc.* , 1992, vol. 114, p. 3499.
5. King-Morris, M.J. and Serianni, A.S., *J. Am. Chem. Soc.,* 1987, vol. 109, p. 3501.
6. Angyal, S.J., *Angew. Chem., Int. Ed. Engl*., 1969, vol. 8, p. 157; Angyal, S.J. and Le, F.R., *Carbohydr. Res*., 1984, vol. 126, p. 15; Angyal, S.J. and Pickles, V.A., *Aust. J. Chem*., 1972, vol. 25, p. 1695.
7. Tobiason, F.I., Swank, D.D., Vergoten, G., and Legrande, P.J., *Carbohydr. Chem*., 2000, vol. 19, p. 959.
8. Serianni, A.S., Wu, J., and Carmichael, I., *J. Am. Chem. Soc*., 1995, vol. 117, p. 8645.
9. Grindley, T.B. and Gulasekharam, V., *J. Chem. Soc., Chem. Commun*., 1978, vol. 23, 1073.
10. Bozo, E., Medgyes, A., Boros, S., and Kuszmann, J., *Carbohydr. Res*., 2000, vol. 329, p. 25.
11. Ferrier, R., Collins, P.M., *Monosaccharide Chemistry*, London: Penguin Books, 1972.
12. Blizzard, A.C. and Santry, D.P., *J. Chem. Phys.*, 1971, vol. 55, p. 950; Blizzard, A.C. and Santry, D.P., *J. Chem. Phys*., 1973, vol. 58, p. 4714.
13. Danilova, V.A. and Krivdin, L.B., *Russ. J. Org. Chem*., 2003, vol. 39, p. 663.
14. Danilova, V.A. and Krivdin, L.B., *Russ. J. Org. Chem*., 2003, vol. 39, p. 1764.

15. Cloran, F., Carmichael, I., and Serianni, A.S., *J. Am. Chem. Soc*., 2001, vol. 123, p. 4781.
16. Becke, A.D., *J. Chem. Phys*., 1993, vol. 98, p. 5648.
17. Lee, C., Yang, W., and Parr, R.G., *Phys. Rev. B*, 1988, vol. 37, p. 785.
18. Hariharan, P.C. and Pople, J.A., *Theor. Chim. Acta*, 1973, vol. 28, p. 213.
19. Krishnan, R., Binkley, J.S., Seeger, R., and Pople, J.A., *J. Chem. Phys*., 1980, vol. 72, p. 650.
20. Dunning, T.H., Jr., *J. Chem. Phys*., 1989, vol. 90, p. 1007.
21. Ramsey, N.F., *Phys. Rev*., 1953, vol. 91, p. 303.
22. Diz, A.C., Ruiz de Azua, M.C., Giribet, C.G., and Contreras, R.H., *Int. J. Quantum Chem*., 1990. vol. 37, p. 663; Contreras, R.H., Giribet, C.G., Ruiz de Azua, M.C., Cavasotto, C.N., Aucar, G.A., and Krivdin, L.B., *J. Mol. Struct. (Theochem)*, 1990, vol. 210, p. 175.
23. Engelmann, A.R., Natiello, M.A., Scuseria, G.E., and Contreras, R.H., *Comput. Phys. Commun*., 1986, vol. 39, p. 409; Engelmann, A.R. and Contreras, R.H., *Int. J. Quantum Chem*., 1983, vol. 23, p. 1033.
24. Coolidge, M.B. and Stewart, J.J.P., *QCPE. Program 455 (Release 6.0)*, 1990.
25. Schmidt, M.W., Baldridge, K.K., Boatz, J.A., Eldert, S.T., Gordon, M.S., Jensen, J.H., Koseki, S., Matsunaga, N., Nguyen, K.A., Su, S.J., Windus, T.L., Dupuis, M., and Montgomery, J.A., *J. Comput. Chem*., 1993, vol. 14, p. 1347.