ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 6, pp. 1212–1213. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © T.G. Volkova, I.O. Sterlikova, Yu.V. Soboleva, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 6, pp. 1035–1037.

Quantum-Chemical Simulation of Acyclic and Cyclic Forms of Glucose in Ethanol

T. G. Volkova[a], I. O. Sterlikova[b], and Yu. V. Soboleva[a]

[a] *Ivanovo State University, Ivanovo, Russia*

[b] *Ivanovo State Medical Academy, ul. Ermara 39, Ivanovo, 153025 Russia*
e-mail: sterlikova75@mail.ru

Received October 28, 2013

Abstract—Equilibrium between acyclic and cyclic forms of glucose in ethanol has been simulated by quantum chemistry methods. The cyclic form prevails in the ethanolic solution. Solvation of glucose molecules is accompanied by additional structurization, the effect being more prominent in the case of the linear form.

Keywords: specific solvation, glucose, tautomerism, quantum-chemical simulation

DOI: 10.1134/S1070363214060267

Mesomorphic carbohydrate-based compounds have been studied for quite a long time. The first report on the unusual behavior of monosaccharides containing a long alkyl fragment dates back to the early 20th century [1, 2]. In the later paper, such compounds have been described as liquid crystals stabilized by hydrogen bonding [3]. Modern studies of liquid crystals containing carbohydrate fragments [4] have revealed that they can possess thermotropic or liotropic properties, depending on the hydrophilic-hydrophobic balance of the molecule.

Conformations of monosaccharides in the crystal form and in the solution are substantially different; therefore, the study of solvent effects on the conformation state is of definite importance. A wide spectrum of experimental and theoretical methods has been applied to determine the monosaccharides conformation in aqueous media [5, 6]. Further interest to studies of carbohydrates hydration has been due to the significant role of the latter in conformation transformations and thermal stabilization of globular proteins [7].

Our interest to this field has emerged from the problem of identification of products of glucose interaction with 4-aminobenzoic acid esters.

Quantum-chemical simulation of solvation of the model molecules (cyclic and acyclic forms of D-glucose) in ethanol was run in the frame of the self-consistent reaction field applying the PCM approach implemented in the GAMESS software [8], using the DFT B3LYP/6-31G method. The simulations were run with the full geometry optimization without any symmetry constrains; the second derivatives matrix was calculated for each stationary point. All discussed structures possessed real vibration frequencies exclusively.

In the crystal state, glucose exists in the form of D-glucopyranose [9–11], whereas various stereoisomeric and conformational transitions are typical of its aqueous solutions [7]. The alkalization or acidification of the monosaccharide solution shifts tautomeric equilibrium between the cyclic and the acyclic forms to the side of the latter [12].

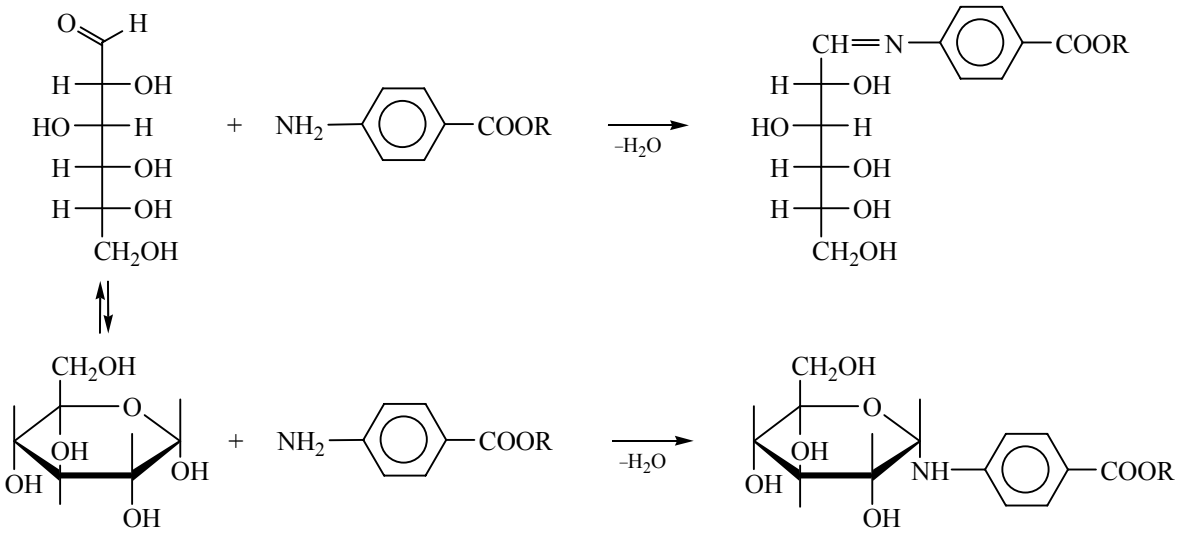
The interaction of glucose with 4-aminobenzoic acid can yield products of the reaction with either

Solvation energy and thermodynamic parameters of glucose tautomeric forms in ethanol[a]

Glucose form	E_{el}, kcal/mol	ΔH_{solv}, kcal/mol	ΔS_{solv}, cal mol^{-1} K^{-1}	ΔG_{solv}, kcal/mol
Acyclic	–20.67	–1.13	–5.38	0.47
Cyclic	–16.26	–4.42	–3.58	–3.39

[a] E_{el} is the energy of electrostatic interaction between the solute and the solvent; ΔH_{solv} includes the zero oscillations energy.

Scheme 1.



cyclic or acyclic glucose form, depending on the one prevailing in the solution (Scheme 1).

The electrostatic term of the solvation energy for both tautomeric forms of glucose is given in the table along with thermodynamic parameters of solvation.

Solvation energy of the acyclic glucose form was more negative.

The equilibrium state in the tautomeric pairs is determined by the forms energy values if their difference is below 4.78 kcal/mol [13]. In the case of the studied tautomeric pair, the energy difference was 7.04 kcal/mol; hence, the cyclic glucose form prevailed in ethanolic solution.

According to the simulation results, solvation of both glucose forms in ethanol was exothermic, the ΔH_{solv} being 4 times lower in the case of the linear form. The entropy term of the solvation free energy was negative, pointing at additional structurization upon solvation, the effect being more prominent in the case of the linear tautomer.

ACKNOWLEDGMENTS

This work was carried out in the frame of Ministry of Education and Science project "Preparation and study of practically important catalysts based on carbon nanomaterials" of the scientific-educational complex "Chemical Physics."

REFERENCES

1. Fischer, E. and Helaerich, B., *J. Lieb. Ann. Chem*., 1911, vol. 383, no. 1, p. 68.
2. Salway, A.H., *J. Chem. Soc*., 1913, no. 103, p. 1022.
3. Noller, C.R. and Rockwell, W.C., *J. Am. Chem. Soc*., 1938, vol. 60, no. 9, p. 2076.
4. Singh, M.K., Xu, R., Moebs, S., Kumar, A., Queneau, Y., Cowling, S.J., and Goodby, J.W., *Chem. Eur. J*., 2013, vol. 19, no. 16, p. 5041. DOI: 10.1002/chem., 201202933.
5. Perelygin, I.S., Kimtis, L.L., Chizhik, V.I., Ermakov, V.I., Trostin, V.N., Yurov, G.S., Abrosimov, V.K., Korolev, V.V., Belousov,V .P., Shutin, S.G., Gol'dshtein, I.P., and Fedotov, A.N., *Eksperimental'nye metody khimii rastvorov: Spektroskopiya i kalorimetriya* (Experimental Methods of Solution Chemistry: Spectroscopy and Calorimetry), Moscow: Nauka, 1995.
6. *Eksperimental'nye metody khimii rastvorov: densimetriya, viskozimetriya, konduktometriya i drugie metody* (Experimental Methods of Solution Chemistry: Densitometery, Viscometry, Conductivity, and Other Methods), Kutepov, A.M., Ed., Moscow: Nauka, 1997.
7. *Biologicheski aktivnye veshchestva v rastvorakh: struktura, termodinamika, reaktsionnaya sposobnost'* (Biological Active Substances in Solutions: Structure, Thermodynamics, Reactivity), MOSCOW: Nauka, 2001.
8. Granovsky, A.A., *PCGAMESS, v. 7.1. http:// classic.chem.msu. su/gran/gamess/index. html.*
9. Brown, G.M. AND Levy, H.A., *Science*, 1965, vol. 147, p. 1038.
10. Mostad, A., *Acta Chem. Scand*., 1994, vol. 48, p. 276.
11. Kouwijzer, M.L.C.E., van Eijck, B.P., Kooijman, H., and Kroon, J., *Acta Cryst. (B),* 1995, vol. 51, no. 2, p. 209.
12. Stepanenko, B.N., *Khimiya i biokhimiya uglevodov: monosakharidy* (Chemistry and Biochemistry of Carbohydrates: Monosaccharides), Moscow: Vysshaya Shkola, 1977.
13. Gornostaev, L.M., *Sorosovsk. Obrazovat. Zh*., 1996, no. 4, p. 33.