CMST 6(1) 61-64 (2000) DOI:10.12921/cmst.2000.06.01.61-64

COMPUTATIONAL METHODS IN SCIENCE AND TECHNOLOGY 6, 61-64 (2000)

THE EFFECT OF DIFFUSE FUNCTIONS FOR PROPER DESCRIPTION OF ENERGIES OF STRUCTURES OF D-GLUCOSE

MARCIN HOFFMANN[1], JACEK RYCHLEWSKI[1,2]

[1] *Quantum Chemistry Group, Faculty ofChemistry, Adam Mickiewicz University,*
ul. Grunwaldzka 6, 60-780 Poznań, Poland
[2] *Institute ofBioorganic Chemistry, Polish Academy of Sciences,*
id. Noskowskiego 12/14, 61-704 Poznań, Poland

Carbohydrates are ofutmost importance for all living organisms [1], Apart form being blood group determinants [2], they are important in many biological processes: cell adhesion [3], hormone-receptor binding [4], lymphocyte homing and migration [5]. Especially D-glucose is involved in energy metabolism and storage [2], Cellulose, composed of D-glucose, builds cell walls and as the major constituent of most plants is particularly interesting as renewable source of energy [6], Monosaccharides and especially D-glucose attracted recently much attention not only form bioorganic but also computational chemists [7-17]. Based on experimental results it is commonly believed that the lowest energy form of D-glucose is six membered cyclic structure of D-glucopyranose. However, the recent computational studies, utilizing density functional theory (DFT) at B3LYP/6-31G** level, performed by B. Ma, H. F. III Schaefer, and N. L. Allinger, indicated that the lowest energy form of D-glucose is FUR1, five membered structure of D-glucofuranose [18], (See Figure 1 and Figure 2). Later, those results were correted by J. H. Lii, B. Ma, and N. L. Allinger at larger basis set 6-311++G(2d,2p) [19], At this basis set the lowest energy structures possesed the usual for D-glucose six membered ring of D-glucopiranose.

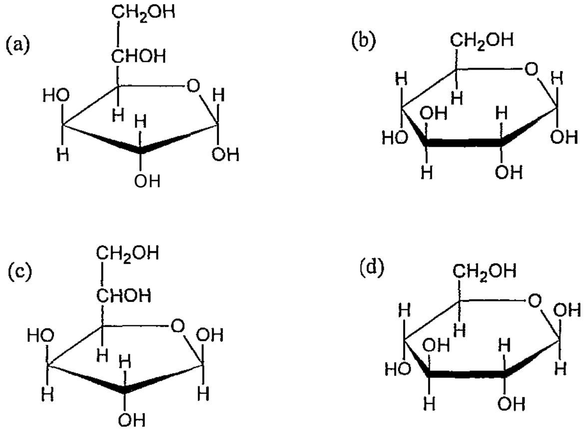


Figure 1. Structures of (a) α-D-glucoiuranose, (b) α-D-glucopyranose,
(c) β-D- glucofiiranose, (d) β-D-glucopyranose

Table I. Relative energies of structures of D-glucose calculated at various levels of theory with the use of different basis sets for geometry optimized at B3LYP/6-31G(d,p)

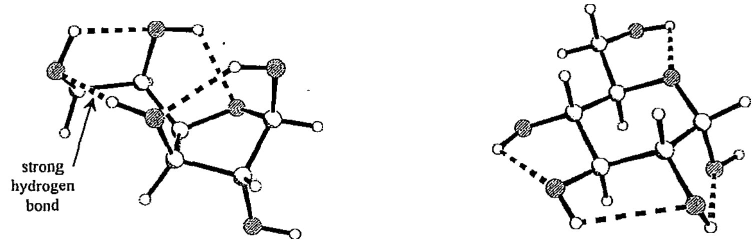
	Basis set	No of funct.	PYR1	PYR2	FUR1	FUR2
B3LYP	6-31G(d)	204	0	0.74	-0.24	0.12
	6-31G(d,p)	240	0	0.65	-0.09	0.33
	6-31+G(d,p)	288	0	0.01	3.67	4.07
	6-31++G(d,p)	300	0	-0.01	3.63	4.03
	cc-pVDZ	228	0	0.92	-0.59	-0.19
	aug-cc-pVDZ	384	0	-0.13	3.80	4.27
	6-311++G(d,p)	348	0	-0.06	3.87	4.36
	6-311++G(3df,3pd)	684	0	-0.10	3.75	4.18
	cc-pVTZ	528	0	0.13	2.51	2.80
	aug-cc-pVTZ	828	0	-0.14	3.85	4.32
MP2	6-31G(d)	204	0	0.58	-1.27	-0.74
	6-311++G(d,p)	348	0	-0.34	3.12	3.93

Initially, the discrepancy between the computed at lower level, and experimental results were attributed to solvent effects, and after calculations at 6-311++G(2d,2p) basis to the influence of the basis set size and basis set superposition error. These findings stimulated our interest and prompted us to study the relative energy of pyranose and furanose rings of D-glucose utilizing various theoretical levels and various basis sets.

According to Ma et al. their FUR1 structure of (3-D-glucofuranose is of 0.23 kcal/mol lower in energy than PYR1 structure of α-D-glucopyranose at B3LYP/6-31G** level. After calculations at 6-311++G(2d,2p) basis set Lii et al. concluded that the PYR1 structure is of 3.34 kcal/mol lower in energy than the FUR1. The results of our calculations with Gaussian94 [20] at different basis sets at B3LYP and MP2 levels are presented in Table I.

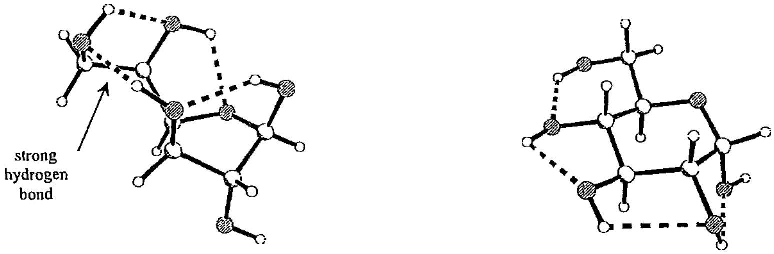
As can be easily concluded from Table I the relative energy of pyranose versus furanose structures is mainly affected, at correlated level, by the inclusion of diffuse functions in the basis set. At MP2/6-31G(d)//B3LYP/6-31G(d,p) the structure FUR1 has the lowest relative energy of -1.27 kcal/mol (in relation to the PYR1 structure). Similarly, at B3LYP/6-31G(d,p) level the structure with furanose ring has relative energy of -0,62 kcal/mol. On the other hand for larger basis set containing diffuse functions - 6-311++G(d,p) - the furanose forms have relative energies of about 4 kcal/mol for MP2 and B3LYP calculations. At 6-311++G(d,p) basis set the lowest energy structures have six membered pyranose rings.

Strong hydrogen bonds can be observed for the FUR1 and FUR2 structures. (See Figure 2). The proton acceptor distances are 1.79 Å and the donor proton acceptor angles are 159.5°. Moreover, oxygen atoms involved in these hydrogen bonds posses strongly negative point charges as obtained according to Mulliken analysis. It appears that the strong electrostatic component of hydrogen bonds observed in FUR1 and FUR2 explains why the addition of diffuse functions to a basis set affects the results so significantly. It is widely accepted that for proper description



FURl

PYR2



FUR2

PYRi

Fig. 2. Perspective view of FUR1, FUR2, PYR1 and PYR2 structures of D-glucose. Dashed lines indicate the presence of hydrogen bonds

of anionic systems diffuse functions are necessary [21]. Therefore in the case of FUR1 and FUR2, the use of diffuse functions is very important for correct description of energies of hydrogen bonds, with oxygen atoms high in negative charge. As the result in basis sets with diffuse functions furanose structures, instead of being the lowest energy ones, become about 4 kcal/mol higher in energy than the pyranose structures.

In the case of B3LYP calculations the addition of one set of diffuse functions centered on non-hydrogen atoms - the 6-31+G(d,p) basis set — renders the relative energy of the furanose structures. At 6-31+G(d,p) basis set both the FUR1 and FUR2 structures are of about 4 kcal/mol higher in energy than PYR1 and PYR2. Addition of the second set of diffuse function centered on hydrogen atoms - 6-31++G(d,p) basis set - does not change further relative energies of furanose and pyranose rings.

Similar effect is observed for cc-pVDZ basis set. At B3LYP/cc-pVDZ level the furanose structures of D-glucose have lower energy than pyranose ones. But at B3LYP/aug-cc-pVDZ (cc-pVDZ basis set augmented with diffuse functions) the furanose structures have relative energy of about 4 kcal/mol in respect to pyranose structures.

At very large basis set cc-pVTZ, B3LYP calculations indicate that the structures with furanose ring have higher relative energy (over 2,5 kcal/mol), but again at aug-cc-pVTZ basis set the FUR1 and FUR2 structures have relative energies about 4 kcal/mol.

All in all, the results of our calculations allow to conclude that for proper description of relative energies of structures of D-glucose, and most probably of other structures with hydrogen bonds, the diffuse functions are of utmost importance. What seems to be particularly important from practical point of view, is that the inclusion of just one set of diffuse functions makes up for most of the difference in relative energies. Therefore the single point energies calculated at 6-31+G(d,p) basis set within B3LYP method are sufficient for comparing the energies of different conformers of larger systems, where basis sets of greater size can not be used due to limited computer resources.

Acknowledgement

The authors are grateful to Prof. U. Rychlewska for allowing the use of the Simens Shelxtl/xp software to prepare drawings. Authors thank Poznan Supercomputing and Networking Center for the access to computer resources therein. One of the authors (M. H.) thanks Foundation for Polish Science for fellowship for young scientists. The financial aid from the Polish Committee for Scientific Research KBN - grants number 8T11F 02815 and T09A17118 is gratefully acknowledged.

References

[1] Colins P., Ferrier R., *Monosacharides: Their Chemistry and Their Roles in Natural Products,* Wiley, New York (1995).

[2] Styer L., *Biochemistry.* W. H. Freeman & Co: New York (1995).

[3] Springer T. A., Nature, **346,** 425 (1990).

[4] Thotakura N. R., Weintraub B. D., Bahl 0. P., Mol. Cell. Endirinol., **70,** 263 (1990).

[5] Stoolman L. M., Cell, **56**, 907 (1989).

[6] Green A. E„ Zanardi, M., Int. J. Quantum Chem., 66, 219 (1998).

[7] Zheng Y.-J., Rick L. O., Leary J. A., J. Mol. Struct. (Theochem), **389,** 233 (1997).

[8] Chung-Phillips A, Chen Y. Y„ J. Phys. Chem., **A103,** 953 (1999).

[9] Wladkowski B. D„ Chenoweth S. A., Jones K. E„ Brown J. W, J. Phys. Chem., **A102,** 5086 (1998).

[10] Simmerling C„ Fox T„ Kollman P. A., J. Am. Chem. Soc., **120,** 5771 (1998).

[11] Cramer C. J., Truhlar D. G„ J. Am. Chem. Soc., **115,** 5745 (1993).

[12] Rockwell G. D„ Grindley T. B„ J. Am. Chem. Soc, **120,** 10953 (1998).

[13] Luque F. J, Lopez J. M, Lopez de la Paz M, Vicent C, Orozco M, J. Phys. Chem, **A102,** 6690 (1998).

[14] Molteni C, Parrinello M, J. Am. Chem. Soc, **120,** 2168 (1998).

[15] Barrows S. E, Storer J. W, Cramer C. J, French A. D, Truhlar D. G, J. Comput. Chem, **19**, 1111 (1998).

[16] Damm W, Frontera A, Tirado-Rives J, Jorgensen W. L, J. Comput. Chem, **18,** 1955 (1997).

[17] Barrows S. E„ Dulles F. J, Cramer C. J, French A. D„ Truhlar D. G„ Carbohydr. Res, 276, 219 (1995).

[18] Ma B, Schaefer III H. F„ AllingerN. L„ J. Am. Chem. Soc, **120**, 3411 (1998).

[19] Lii J. H„ Ma B, AllingerN. L„ J. Comput. Chem, **20**, 1593 (1999).

[20] Gaussian 94, Revision E.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, **J.** Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. **J.** Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA (1995).

[21] Herhe W. J, Radom L, Schleyer P.v. R, People J. A, *Ab initio Molecular Orbital Theory.* Wiley, NewYork (1986).