

## DFT STUDY OF LONG BONDS IN RADICAL CATIONS OF SUGAR DERIVATIVES

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### Abstract

We have performed DFT computations on radical cations of several monosaccharide derivatives, using the STO-3G and 3-21G basis sets. The obtained long bond lengths were compared with the values we have previously obtained using the RM1 and PM7 semi-empirical methods. The applied DFT methods offered smaller values for the long bond lengths, attaining only 1.6÷1.7 Å. Also, in contrast with the simple STO-3G basis set, which shows some exceptions, the more advanced 3-21G basis set always places the long bond in the correct C4-C5 position, as suggested by the EI-MS analyses.

### Introduction

Long bonds appear to be a ubiquitous feature in the molecular radical cations produced during the positive mode electron ionization mass spectrometry (EI-MS) analysis of compounds possessing vicinal electron donor substituents, like diols or diethers [1]. Carbohydrates are an example of such compounds. While semi-empirical methods [2,3] give long bond lengths for radical cations that are likely to be exaggerated, DFT computations are known to be more moderate in this respect. To verify this assumption we have performed DFT analyses on radical cations of five monosaccharide derivatives, which contain the furanose moiety (**Fig. 1**): 1,2:5,6-di-*O*-isopropylidene- $\alpha$ -D-glucofuranose (DAG), 1,2:5,6-di-*O*-isopropylidene- $\alpha$ -D-allofuranose (DAAlo), 1,2:5,6-di-*O*-isopropylidene- $\alpha$ -D-galactofuranose (DAGal), 2,3:5,6-di-*O*-isopropylidene- $\alpha$ -D-mannofuranose ( $\alpha$ -DAM) and 2,3:5,6-di-*O*-isopropylidene- $\beta$ -D-mannofuranose ( $\beta$ -DAM). All these species show, during the EI-MS analysis, a preference for the breaking of the C4-C5 bond, with the formation of the 2,2-dimethyl-1,3-dioxolan-4-ylum oxocarbenium ion, which exhibits a high intensity  $m/z = 101$  peak [2,3].

### Experimental

All structures were initially modeled using the HyperChem 8.0.10 software [4]. The starting neutral molecules, obtained after “MM+” pre-optimization, were optimized with the RM1 semi-empirical method [5]. The radical cations were obtained from these structures and were pre-

optimized with RM1. As for “Spin Pairing”, RHF operators were used for neutral molecules, while UHF operators were employed for radical-cations. The SCF “Convergence limit” was set at  $10^{-5}$ , without using the “Accelerate convergence” procedure. For geometry optimization, the “Polak-Ribière (conjugate gradient)” algorithm was selected with a RMS gradient of  $0.01 \text{ kcal} (\text{Å mol})^{-1}$ , the molecules being considered in vacuum (conditions similar to those found in EI-MS detectors).

Theoretical calculations were finally performed using the Gaussian 09 software [6]. The equilibrium geometries of the radical cations were optimized using the density functional theory (DFT) method at the B3LYP/STO-3G or B3LYP/3-21G levels. The B3LYP hybrid functional was used for these studies because of convention and the successful use to model a range of gas-phase reactions.

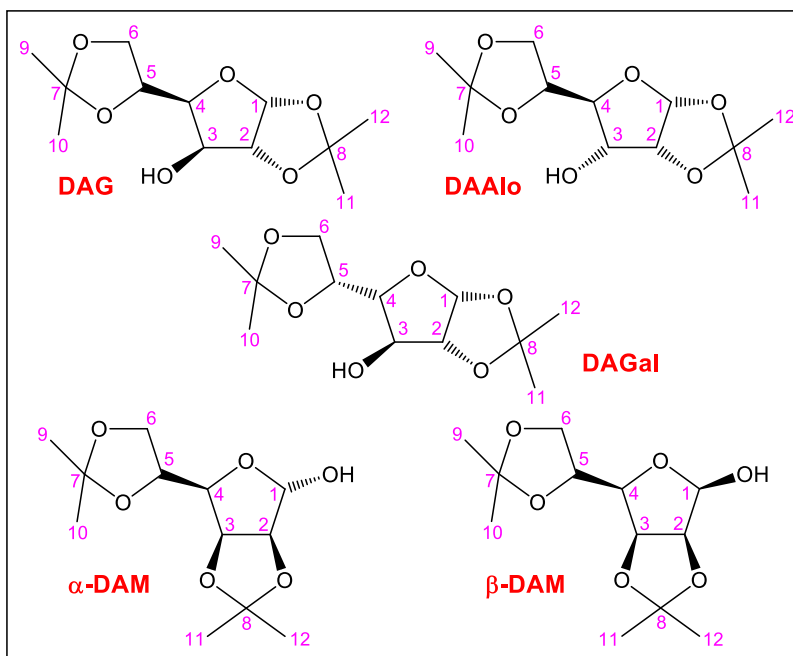


Figure 1. Structure of the studied compounds

## Results and discussion

The DFT results regarding the enthalpy of formation ( $\Delta_f H^0$ ) at 0 and 298.15 K, the Gibbs free energy ( $\Delta_f G^0$ ) at 298.15 K and some bond lengths are given in **Tables 1** and **2**, while the O4-C4-C5, O5-C5-C4 and O4-C4-C5-O5 angle values are given in **Table 3**.

Table 1. Results obtained for the radical cations using the B3LYP/STO-3G level of theory

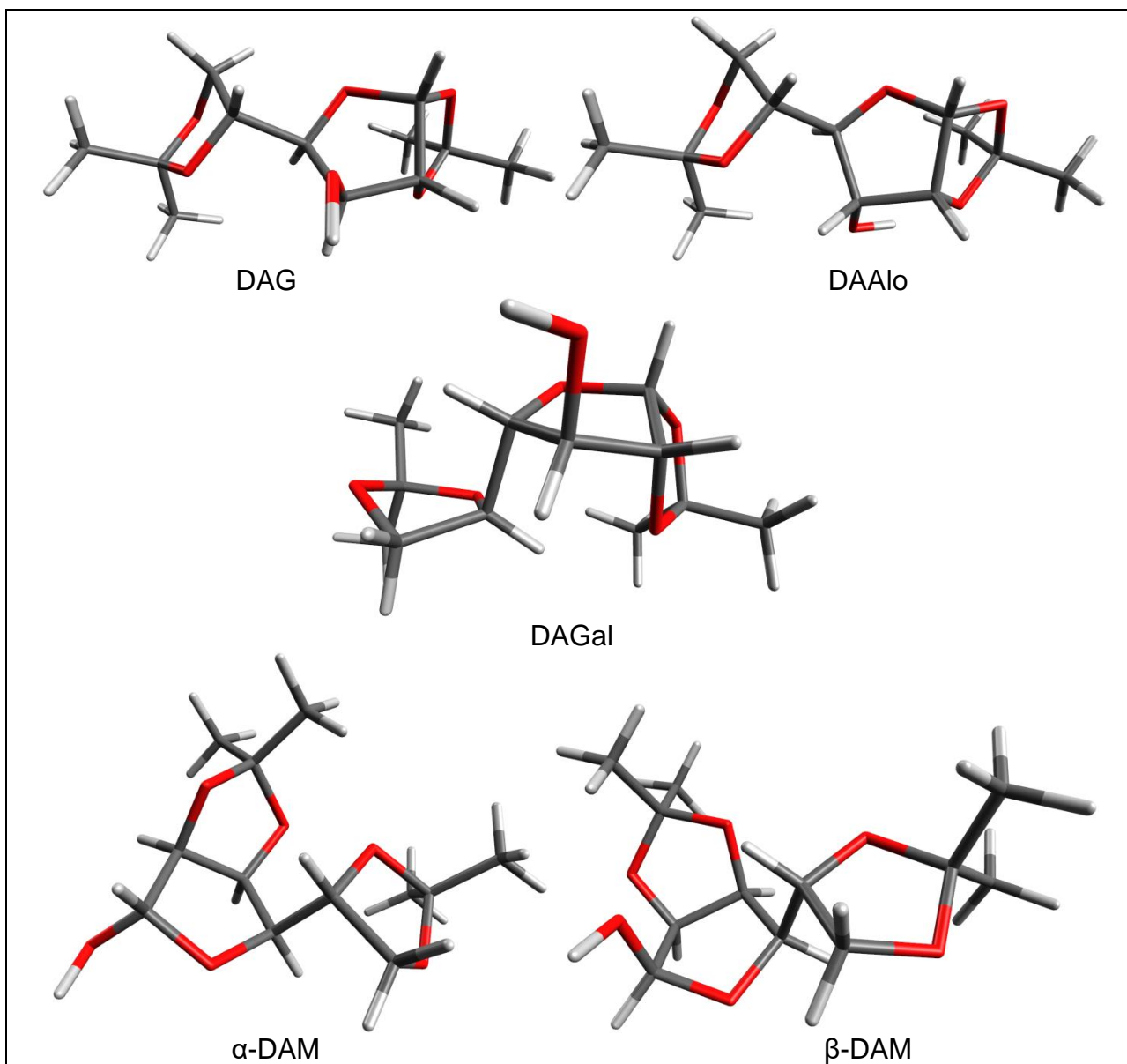
Compound	$\Delta_f H^0$ 0 K (kcal mol <sup>-1</sup> )	$\Delta_f H^0$ 298 K (kcal mol <sup>-1</sup> )	$\Delta_f G^0$ 298 K (kcal mol <sup>-1</sup> )	Bond length (Å)				
				C1-C2	C2-C3	C3-C4	C4-C5	C5-C6
DAG*	-1967.33	-1984.8	-2311.0	1.583	1.594	1.613	<b>1.637</b>	1.575
DAAlO	-1977.86	-1996.1	-2324.1	1.576	1.589	1.606	<b>1.628</b>	1.574
DAGal	-1961.96	-1979.3	-2305.4	1.586	<b>1.635</b>	1.585	1.617	1.580
$\alpha$ -DAM	-1969.30	-1987.0	-2314.2	1.586	1.575	1.592	<b>1.619</b>	1.573
$\beta$ -DAM	-1972.65	-1990.7	-2319.0	1.595	1.581	1.585	<b>1.609</b>	1.566

\*optimization was started from 3-21G geometry

**Table 2.** Results obtained for the radical cations using the B3LYP/3-21G level of theory

Compound	$\Delta_f H^0$ 0 K (kcal mol <sup>-1</sup> )	$\Delta_f H^0$ 298 K (kcal mol <sup>-1</sup> )	$\Delta_f G^0$ 298 K (kcal mol <sup>-1</sup> )	Bond length (Å)				
				C1-C2	C2-C3	C3-C4	C4-C5	C5-C6
DAG	-1250.31	-1267.4	-1592.9	1.536	1.529	1.538	<b>1.650</b>	1.531
DAAlo	-1254.74	-1272.5	-1599.7	1.542	1.553	1.572	<b>1.648</b>	1.541
DAGal	-1250.40	-1267.8	-1594.7	1.536	1.527	1.548	<b>1.712</b>	1.534
$\alpha$ -DAM	-1250.86	-1268.4	-1595.7	1.527	1.547	1.562	<b>1.562</b>	1.537
$\beta$ -DAM	-1252.40	-1269.9	-1597.0	1.553	1.556	1.556	<b>1.597</b>	1.537

The molecular models for the considered radical cations (B3LYP/3-21G) are shown in **Fig. 2**.

**Figure 2.** Molecular models obtained after running the B3LYP/3-21G optimization

The observed position of the long bond generally coincides with our previous results obtained using the RM1 and PM7 semi-empirical methods.

**Table 3.** Angle values (degrees) obtained for the studied radical cations

Compound	STO-3G			3-21G		
	O4-C4-C5	O5-C5-C4	O4-C4-C5-O5	O4-C4-C5	O5-C5-C4	O4-C4-C5-O5
DAG	113.4	108.1	117.6	105.8	105.3	176.2
DAAlO	115.8	108.2	-134.7	111.1	108.3	-162.1
DAGal	112.6	111.6	71.2	112.1	108.5	-42.7
$\alpha$ -DAM	112.5	110.7	-138.5	107.3	110.2	-161.5
$\beta$ -DAM	110.7	110.2	-143.5	109.5	107.5	166.8

### Conclusion

In contrast with our previous results [2,3] obtained using the RM1 and PM7 semi-empirical methods, which give long bonds of slightly over 2 Å, the DFT methods applied offered long bonds of maximum 1.712 Å. The 3-21G basis set seems to give better results with respect to the long bond location, when compared with the more simple STO-3G basis set.

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