LONG BONDS IN RADICAL CATIONS OF SORBITOL AND MANNITOL

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Abstract

The quantum chemical analysis (RM1 semiempirical method) of sorbitol and mannitol in their radical cation states reveals C-C long bonds with lengths around 2.1 or 2.2 Å. In some cases, the stabilities of these long bonds appear to be related with the intensities of the corresponding peaks found in the mass spectra of these hexitols.

Introduction

Sorbitol and mannitol belong to the chemical family of sugar alcohols, or the broader category of polyols (particularly hexitols). Polyols are polyhydric alcohols derived through chemical reduction (hydrogenation) of reducing sugars. Most of the commercially important polyols are produced by chemical hydrogenation of their corresponding reducing sugars. For example, sorbitol is produced by hydrogenation of dextrose (glucose), while mannitol is derived through fructose hydrogenation [1].

Alongside monosaccharide sugars, polyols are carbohydrate materials of considerable commercial value and interest to the commercial food sector. Besides their role of food nutrients and sweeteners, they also provide specific functional properties in manufactured food products [1].

Sorbitol belongs to the group of naturally occurring hexitols. In fruit and leaves, sorbitol is formed as a biochemical intermediate in the synthesis of starch, cellulose, sorbose, or vitamin C. In animals, sorbitol can be detected as an intermediate in the absorption of glucose or the formation of fructose via glucose. Sorbitol is produced on a large scale by means of the catalytic hydrogenation of D-glucose (dextrose) [2].

D-Mannitol is a hexitol derived from D-mannose. D-Mannitol is widely distributed in nature, occurring in olive trees, plane trees, and fruit and vegetables. It is also naturally found in some edible fungi and Laminaria species seaweed (marine algae, especially brown algae, containing 10–20% mannitol, depending on the time of harvest). Furthermore, a large number of fungi and bacteria can produce this polyol from glucose, fructose, or sucrose [2].

In this paper we investigate, using computational methods, the presence of C-C long bonds in the radical cations of sorbitol and mannitol and the possibility of a relation between the intrinsic stability of such long bonds and the intensity of some peaks found in the mass spectra of the two compounds.

Experimental

The molecules of sorbitol and mannitol were initially modelled using the *HyperChem* software [3]. After the "Add H & Model Build" command, the starting neutral molecules were pre-optimized using the MM+ force field and then optimized with the RM1 semiempirical method [4]. The radical cations (formal charge "+1", spin multiplicity "2")

were obtained from these structures and were finally optimized with the RM1 semiempirical method. 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" feature. For geometry optimization and $\Delta_f H$ calculation, the "Polak-Ribière (Conjugate gradient)" algorithm was selected with a RMS gradient of 0.01 kcal/(Å mol), the molecules being considered in vacuum (conditions similar to those found in the EI-MS detectors). The radical cation molecular graphs showing the total spin density were plotted using the "Wire mesh" rendering (carbon – cyan, hydrogen – white, oxygen – red, positive spin density – green wire mesh, and negative spin density – violet wire mesh).

The EI-MS spectral data for sorbitol and mannitol were downloaded from the *NIST Chemistry WebBook* site [5] and visualized using the *ACD/Labs 6.00* software, while the exact masses, the molecular weights and the *m/z* values given under the chemical formulas are those predicted by the *ChemBioDraw Ultra* (v. 12.0) program (included in the *ChemBioOffice 2010* software).

Results and discussion

The EI-MS spectra of sorbitol and mannitol are shown in Fig. 1, while their chemical structure and five possible fragmentations, which are responsible for some of the EI-MS peaks, are shown in Figs. 2 and 3. The intensity of these peaks are shown in Tables 1 and 2.
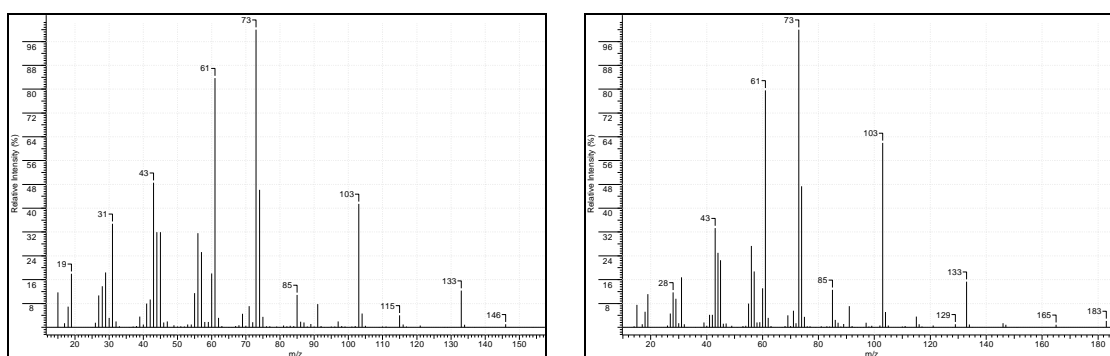

Figure 1. EI-MS spectrum of sorbitol (left) and mannitol (right)

Chemical Formula: $C_6H_{14}O_6$
Exact Mass: 182.08
Molecular Weight: 182.17
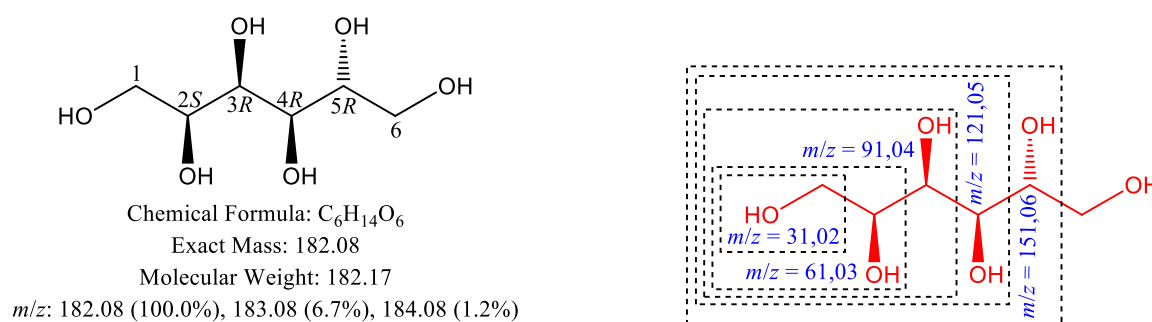*m/z*: 182.08 (100.0%), 183.08 (6.7%), 184.08 (1.2%)

Figure 2. Left: chemical structure of sorbitol (with carbon chain numbering and optical configurations); right: five possible EI-MS fragmentations

Chemical Formula: $C_6H_{14}O_6$
Exact Mass: 182.08
Molecular Weight: 182.17
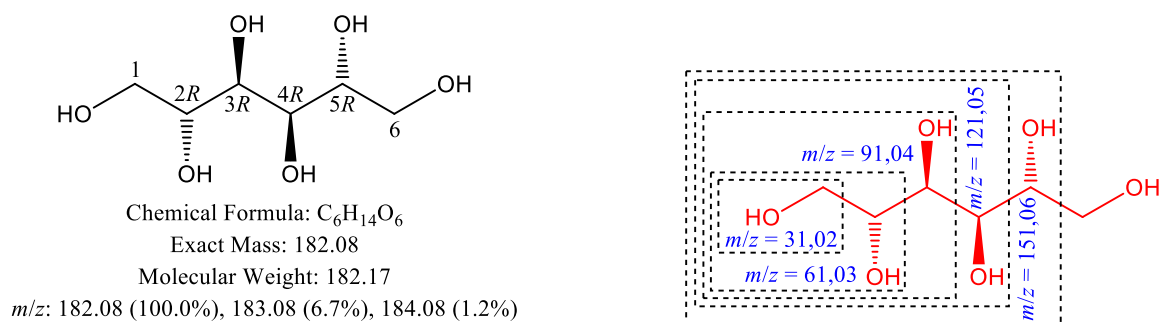*m/z*: 182.08 (100.0%), 183.08 (6.7%), 184.08 (1.2%)

Figure 3. Left: chemical structure of mannitol (with carbon chain numbering and optical configurations); right: five possible EI-MS fragmentations

Table 1. Intensity of target peaks for sorbitol

m/z	RI (%)	TIC (%)
31	34.793	4.937
61	83.698	11.877
91	7.791	1.105
121	0.600	0.085
151	0	0

Table 2. Intensity of target peaks for mannitol

m/z	RI (%)	TIC (%)
31	16.792	2.754
61	79.598	13.055
91	7.091	1.163
121	0.600	0.098
151	0.100	0.016

The ball-and-stick model of different variants of radical cations, obtained by using the RM1 semiempirical method, are shown in Figs. 4 (sorbitol) and 5 (mannitol). The position of the long bonds is clearly established using the green wire mesh, which shows the total spin density. The C-C bond lengths, together with heat of formation values for the neutral species and the various forms of radical cations, are presented in Tables 3 and 4.
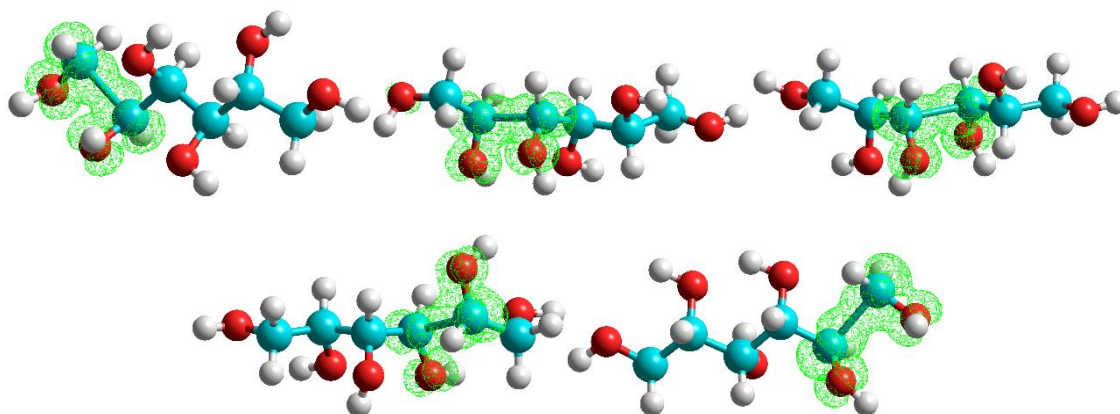

Figure 4. Ball-and-stick model of different variants of radical cations of sorbitol (numbering of carbon atoms starts from left)
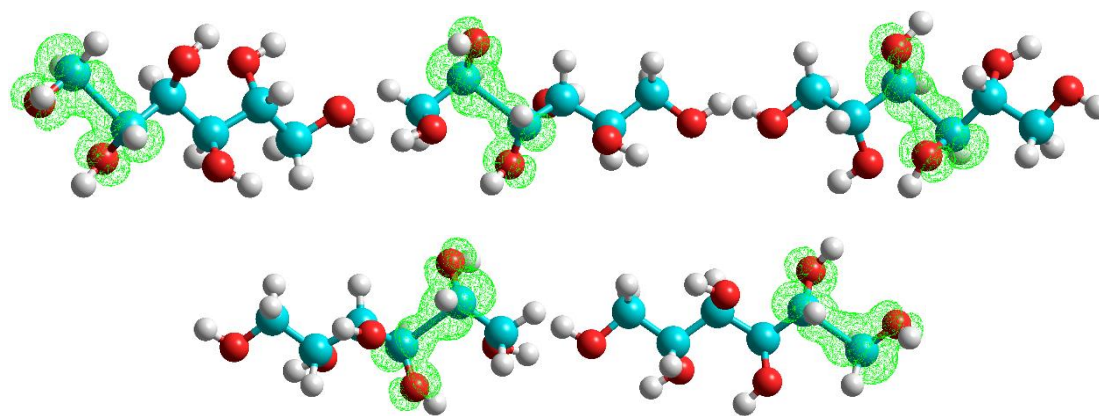
Figure 5. Ball-and-stick model of different variants of radical cations of mannitol (numbering of carbon atoms starts from left)

Table 3. Sorbitol: C-C bond lengths and heats of formation for the neutral molecule and for the radical cation (the most stable form is shown in red)

Bond	Neutral molecule		Radical cation	
	Length (Å)	$\Delta_f H$ (kcal/mol)	Length (Å)	$\Delta_f H$ (kcal/mol)
C1-C2	1.538		2.100	650.946
C2-C3	1.539		2.084	652.723
C3-C4	1.542	446.909	2.122*	651.854*
C4-C5	1.543		**2.167**	**648.572**
C5-C6	1.538		2.101	652.330

*MM+ pre-optimization of radical cation

Table 4. Mannitol: C-C bond lengths and heats of formation for the neutral molecule and for the radical cation (the most stable form is shown in red)

Bond	Neutral molecule		Radical cation	
	Length (Å)	$\Delta_f H$ (kcal/mol)	Length (Å)	$\Delta_f H$ (kcal/mol)
C1-C2	1.536		2.110	656.222
C2-C3	1.543		2.179	651.038
C3-C4	1.543	450.572	2.145	651.544
C4-C5	1.543		**2.180**	**651.038**
C5-C6	1.536		2.110	656.222

For both hexitols it can be seen that, among the five considered EI-MS peaks, the one from m/z 61 shows the highest intensity, in relation to the preferred long bond position at C4-C5 (or, with the same heat of formation value, at C2-C3 for mannitol), which gives for the radical cation the lowest heat of formation.

In the case of sorbitol, this is followed by m/z 31, corresponding to the breaking at C1-C2, while the breaking at C3-C4 shows the lowest probability, according to the higher heat of formation value for the corresponding radical cation.

For mannitol, the reverse was found for the cleavages at C1-C2 or C5-C6 and, respectively, C3-C4. However, the particularly high value for the heat of formation in the case of C1-C2 or C5-C6 fragmentations could indicate that these might not be the ground states of these radical cations, and more work would be required in order to geometrically optimize these structures.

Conclusion

The present computational study has proved the existence of C-C long bonds (around 2.1 or 2.2 Å) in radical cations of sorbitol and mannitol. Also, a relation with the intensity of some mass spectrometric peaks for the two compounds was established.

Acknowledgements

References

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