Correlation Between ^{13}C NMR Chemical Shift, Fractional Charge and Carbon Atom Core Energy in Carbohydrates

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Recently, an *ab initio* study of α- and β-D-glucopyranose and β-maltose was published.[1] Among many details investigated were 1s core energies and fractional atomic charges according to Mulliken population analysis. The carbon atoms fall into three classes, primary, secondary and anomeric; this classification comes about in a purely theoretical way.

A similar pattern is found for the chemical shift in ^{13}C nuclear magnetic resonance. Definitive assignments of the two glucoses and maltose are given by Colson *et al.*[2] It would seem worthwhile to try to establish a correlation with the theoretical results, which, so far as has been found, represent the hitherto most comprehensive *ab initio* calculations on carbohydrates.

The calculated data pertain to the energetically most favourable conformers of α- and β-D-glucopyranose, as found by conformational energy minimization in a potential energy function including all degrees of freedom,[3,4] and to the two thermodynamically most stable conformers of β-maltose, found within the same potential energy function.[5]

In Table 1 the ^{13}C chemical shifts measured in D$_2$O relative to external TMS,[2] carbon atoms fractional charges[1] and C1s energies[1] are compiled. The correlations are seen more clearly in Fig. 1. They are very pronounced for charges, much less for core energies. Regression lines are drawn for the charge correlation; this is hardly worthwhile for the core energy. The line correlating chemical shift and charge for all three classes of carbon atoms has the equation $\delta = 95.4q + 76.24$ or $q = 0.0105\delta - 0.799$, with a correlation coefficient of 0.972.

A similar correlation is found for small alkanes. Gas-phase ^{13}C NMR chemical shifts for ethane and propane relative to methane were recently reported by van de Ven and de Haan.[6] Correlation with carbon charges of methane[7] and ethane[8] calculated with large basis sets gives $\delta = 111.7q + 16.30$ or $q = 0.0090\delta - 0.146$. The slope is close to that for the carbohydrates; the offset, corrected by -52.69 ppm to DMSO-d_6 external[6] and by $+39.56$ ppm to TMS internal,[9] is 3.17. The large difference from 76.24 would be ascribed to solvent effect and change of state.

When hydrogen bonding is to be accounted for in conformational energy calculations, consideration of charge interactions is indispensable, and the monopole approximation is the most expedient technique.[10] This approach has recently been used to describe *intra*-molecular hydrogen bonding in three disaccharides.[11,12] The correlation suggests that estimates of carbon atom charges may be provided by ^{13}C chemical shift measurements.

Table 1. ^{13}C chemical shift, charge and carbon atom core energy in α- and β-D-glucopyranose and two conformers of β-maltose.

	δ	q	C1s	δ	$q(1)$	$q(2)$	C1s(1)	C1s(2)
	β-glc			mal, β-ring				
C1	97.0	+0.210	−11.511	97.1	+0.200	+0.200	−11.493	−11.493
C2	75.2	−0.012	−11.455	75.2	−0.020	−0.012	−11.436	−11.439
C3	77.0	−0.010	−11.456	77.3	−0.001	−0.007	−11.435	−11.439
C4	70.7	−0.018	−11.455	78.1	+0.010	+0.003	−11.436	−11.438
C5	76.8	−0.009	−11.461	75.7	+0.004	−0.000	−11.446	−11.446
C6	61.8	−0.182	−11.452	61.8	−0.174	−0.189	−11.431	−11.436
	α-glc			mal, α-ring				
C1′	93.1	+0.187	−11.509	100.8	+0.210	+0.208	−11.493	−11.504
C2′	72.5	−0.008	−11.458	73.8	−0.010	−0.017	−11.445	−11.449
C3′	73.8	−0.001	−11.453	74.1	−0.011	−0.008	−11.441	−11.450
C4′	70.7	−0.017	−11.451	70.5	−0.012	−0.011	−11.443	−11.450
C5′	72.5	−0.012	−11.456	72.8	+0.003	−0.002	−11.448	−11.453
C3′	61.7	−0.182	−11.449	61.7	−0.176	−0.177	−11.443	−11.446

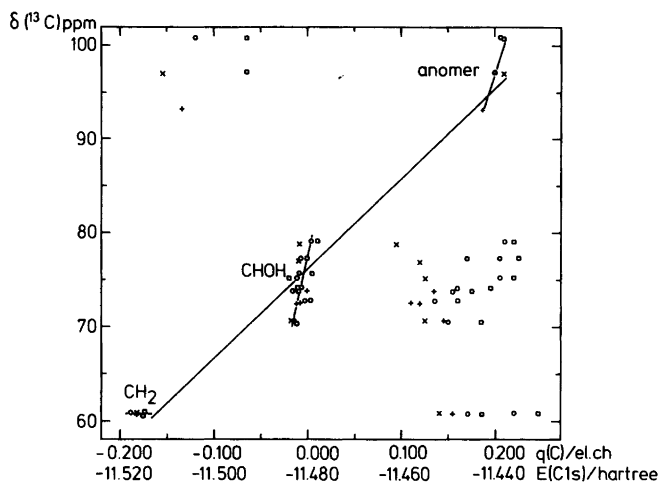*Fig. 1.* Correlations of $\delta(^{13}C)$ with carbon atom charge and $1s$ energy for α- and β-D-glucopyranose and two conformers of β-maltose. $+$, α-glc; $\times$, β-glc; $\square$, mal(1); $\bigcirc$, mal(2).

Estimates obtained in this way, rough though they are, would be quite adequate for providing the electrostatic part of a potential energy function, which would contribute to realistic prediction of conformer geometry by energy minimization.

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