Note

Electronic charge distribution in mono, di, and polysaccharides*

N. YATHINDRA AND V. S. R. RAO†
Centre of Advanced Study in Physics, University of Madras, Guindy Campus, Madras-25, (India)

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Recently, the calculation of conformational energies has become regarded as a valid approach for determining molecular conformations, and many important results have been obtained in the field of carbohydrate chemistry[1–14]. To compute the total conformational energy, nonbonded interactions, electrostatic interactions, torsional strain, hydrogen-bond interactions, and bond-length and bond-angle distortions have to be considered. The form of the potential functions to be used to take these interactions into account have now been well established. Electrostatic interaction energies were, however, neglected in most of the earlier studies in carbohydrates[1–9], probably because of the non-availability of electronic charge values for these molecules. Recent calculations have indicated the importance of such interactions in the random-coil conformations of polypeptides[15], polylactic acids[15] and amylose[10,11], and in assigning favoured conformations for the free sugars[12].

The present work involves the computation of electronic charge-distribution, following the LCAO–MO method of Del Re[16,17], for twelve different types of molecular fragment, including di- and tri-saccharides having various types of linkages. The purpose was to assign more-exact electronic charges for the sugar moieties in a variety of disaccharides, and polysaccharide chains, differing in the type of linkage and the repeating unit.

RESULTS AND DISCUSSION

Figures 1a and 1b show the distribution of σ-charge in a pentopyranose and hexopyranose, respectively. When these sugars are joined through (1→4), (1→3), and (1→2) linkages to form disaccharides, the charge on C-1, and the other carbon atom involved in the glycosidic linkage (C-4′, C-3′, C-2′ as the case may be), shows a decrease by about 0.01 unit from values for corresponding atoms of the free sugar

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[*] Contribution No. 349 from the Centre of Advanced Study in Physics, University of Madras, Madras, India.

[†] To whom inquiries should to be made.

adjacent to the interglycosidic oxygen atom. The charge on the interglycosidic oxygen atom is about −0.264, the same as that on O-5. Very minor changes were also observed, but only at C-2, H-1, and O-5 of the non-reducing residue. This result shows that propagation of charge is not significant beyond the second neighbour from the site of substitution.

As the charge on an atom is not significantly affected by the nature of atoms beyond the second neighbour, the σ-charge distribution on each sugar residue of a polysaccharide must be essentially identical to that of the middle residue of a trisaccharide. Therefore, to determine the charges for a sugar residue in a polysaccharide chain, calculations were made on the corresponding trisaccharide. The charges thus estimated for the atoms of sugar residues in (1→4), (1→3), and (1→2)-linked polysaccharides are given in Tables I and II. The partial, electronic charges shown in columns 2 of Table 2 for (1→4)-linked hexose polysaccharides differ considerably

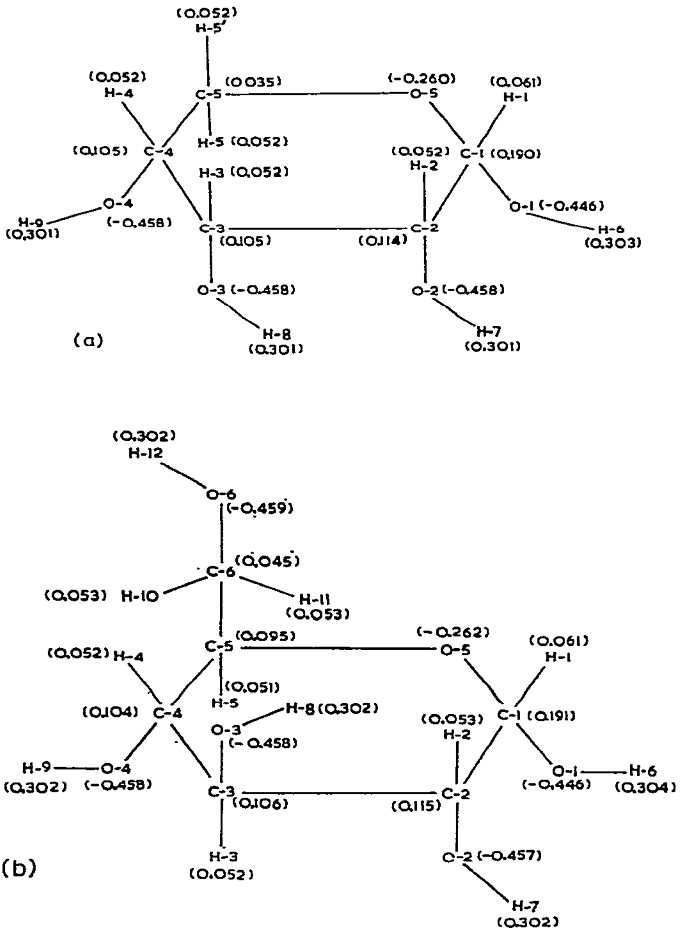

Fig. 1. a, Electronic charges in a pentopyranose; b, electronic charges in a hexopyranose.

from the values assigned from bond dipoles by Goebel[10] *et al.* This discrepancy may be due to the consideration of inductive effects in Del Re's method. It is also noteworthy, from Figures 1a and 1b and Tables I and II that, in polysaccharides, the σ-charges on carbon atoms involved in the glycosidic linkage and the interglycosidic oxygen atoms alone differ significantly from those of the corresponding atoms in monosaccharides. It can also be seen from Tables I and II that there is a traceable pattern in the distribution of σ-charges in the sugar residues of polysaccharides that differ in their type of linkage. Although these results are a natural consequence of Del Re's method and its hypothesis, it is empirically useful to actually point out the range of charge that a atom can have. For example, the hydrogen atom of a C–H bond, except the hydrogen atom attached to the anomeric carbon atom, has a charge of about 0.05 units, and an O–H bond about 0.30. The hydrogen atom attached to the anomeric carbon (C-1) atom has a charge slightly higher than the rest of the hydrogen atoms of the C–H bonds. The ring-oxygen and linkage oxygen-atom have a charge of about −0.26. The hydroxyl oxygen atom has a charge of about −0.46, and the anomeric carbon atom has a charge of approximately 0.18.

TABLE I

σ-CHARGES FOR A SUGAR RESIDUE IN A PENTOSE POLYSACCHARIDE CHAIN

Atom	*Type of linkage*		
	(1→4)	*(1→3)*	*(1→2)*
C-1	0.178	0.178	0.176
C-2	0.113	0.113	0.101
C-3	0.105	0.094	0.105
C-4	0.093	0.104	0.105
C-5	0.035	0.035	0.035
O-1	−0.264 (L)[a]	−0.263 (L)[a]	−0.263 (L)[a]
O-2	−0.457	−0.457	−0.263 (L)[a]
O-3	−0.458	−0.263 (L)[a]	−0.458
O-4	−0.264 (L)[a]	−0.458	−0.458
O-5	−0.263	−0.263	−0.263
H-1	0.060	0.060	0.059
H-2	0.053	0.053	0.051
H-3	0.052	0.051	0.052
H-4	0.050	0.052	0.052
H-5	0.051	0.052	0.052
H-7	0.302	0.302	
H-8	0.302		0.301
H-9		0.301	0.301
H-5*	0.051	0.052	0.052

[a] L denotes the interglycosidic oxygen atom. Atoms are numbered as given in Fig. 1a.

TABLE II

σ-CHARGES FOR A SUGAR RESIDUE IN A HEXOSE POLYSACCHARIDE CHAIN

Atom	*Type of linkage*		
	(1→4)	*(1→3)*	*(1→2)*
C-1	0.178	0.178	0.176
C-2	0.113	0.112	0.101
C-3	0.105	0.094	0.105
C-4	0.092	0.103	0.104
C-5	0.094	0.095	0.095
C-6	0.045	0.045	0.045
O-1	−0.264 (L)[a]	−0.264 (L)[a]	−0.263 (L)[a]
O-2	−0.457	−0.457	−0.263 (L)[a]
O-3	−0.458	−0.264 (L)[a]	−0.458
O-4	−0.264 (L)[a]	−0.459	−0.458
O-5	−0.264	−0.264	−0.264
O-6	−0.457	−0.456	−0.456
H-1	0.060	0.060	0.059
H-2	0.053	0.052	0.051
H-3	0.052	0.051	0.052
H-4	0.050	0.051	0.052
H-5	0.051	0.051	0.051
H-7	0.302	0.302	
H-8	0.301		0.301
H-9		0.301	0.301
H-10	0.053	0.053	0.053
H-11	0.053	0.053	0.053
H-12	0.302	0.302	0.302

[a] L denotes the interglycosidic oxygen atom. Atoms are numbered as given in Fig. 1b.

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