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THE NON-BONDED INTERACTIONS IN D-GLUCOSE AND β-MALTOSE: AN *ab initio* STUDY OF CONFORMATIONS PRODUCED BY EMPIRICAL FORCE-FIELD CALCULATIONS

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ABSTRACT

Minimal basis set SCF-MO computations on conformations of α-D-glucopyranose, β-D-glucopyranose, and β-maltose resulting from empirical energy minimisation reproduce known trends in relative energy. Analysis of electron population and molecular orbital valency-state energy leads to separation of atoms into classes, two for oxygen, three for carbon, and two for hydrogen, the classes being correlated with the chemical environments of the atoms. Partitioning of the total energy into two-centre terms gives a quantification of non-bonded interactions, leading to potential-energy curves for interactions of all types of atom present. Peculiar details of the electronic structure at and around the anomeric carbon atoms are noted: C(1s) chemical shift is insensitive to configuration, but depends on conformation.

INTRODUCTION

As part of a project aimed at a consistent description of conformations and thermodynamic properties of carbohydrates and their derivatives, we have performed *ab initio* calculations on two monosaccharides and one disaccharide. Following SCF-MO computations, we have analysed the total energy by using the concept of bond-energy analysis (BEA) due to Clementi[1].

We had two aims with the work to be reported here. One was to investigate how well our former calculations[2-4], using a purely classical approach with a simple model function for the total potential energy, the consistent force-field (CFF) technique[5], would correspond with fairly extensive quantum-chemical computations in the Roothaan framework. The other was to derive functions for interactions between atoms not bound to each other. In addition, we offer some comments on the electronic structure of the anomeric carbon atom.

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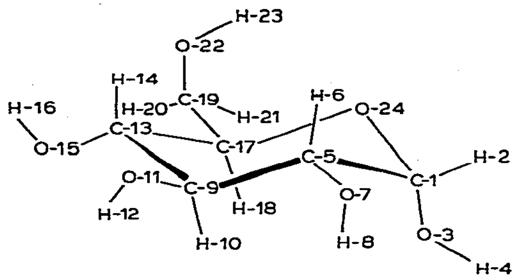

Fig. 1. α-D-Glucopyranose, with atom numbering for computational purposes.

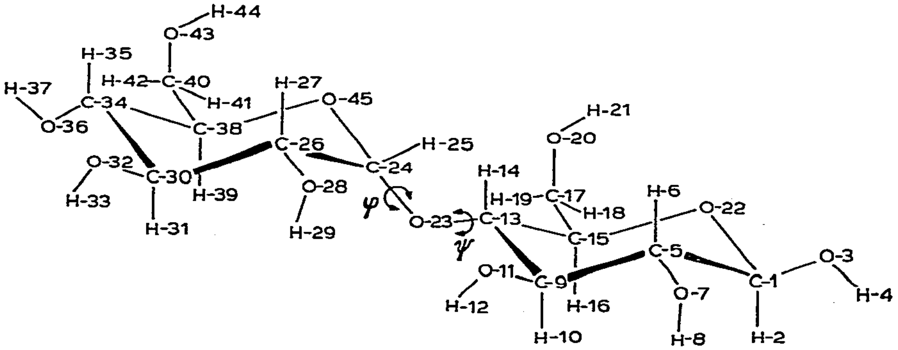

Fig. 2. β-Maltose, with atom numbering for computational purposes.

Two pairs of molecules were chosen: the equilibrium conformations of α- and β-D-glucose in the pyranoid form, and two conformers of β-maltose, which is composed of an α- and a β-D-glucopyranose ring joined by an α-(1→4)-glycosidic linkage.

For the sake of later reference, α-D-glucopyranose and one conformer of maltose are shown in Figs. 1 and 2, with the atomic numbering used in all our computations. In a previous paper[4], β-maltose was shown with the standard carbohydrate numbering.

We have found no references to earlier *ab initio* calculations on these rather large molecules. Jeffrey *et al.* have investigated the geometrical consequences of conformational changes around a carbon atom bound to two oxygen atoms in methanediol[6], methoxymethanol[7], and dimethoxymethane[8]. For these model compounds of carbohydrates, they performed partial geometry optimisation and were able to reproduce the shortening of the anomeric C–O bond. By varying torsional angles and otherwise keeping the internal geometry constant, they derived potential-energy surfaces over torsional angles, and used them to reproduce conformations of pyranosides.

Earlier empirical and semiempirical calculations on the same system, as well as structural studies, are summarised in our previous work[2–4].

TABLE I

GAUSSIAN BASIS SETS FOR H, C, AND O ATOMS

Atom	*No.*	*Type*	*Exponent*	*Contraction*	*Hartree–Fock energy (hartree)*	*Hartree–Fock limit*[16] *(hartree)*
H	1	s	4.50180	0.070452	−0.496979(^2S)	−0.50000
	1	s	0.681444	0.407826		
	1	s	0.151398	0.647752		
C	1	s	1267.18	0.005446	−37.609542(^3P)	−37.68866
	1	s	190.604	0.040526		
	1	s	43.2477	0.179789		
	1	s	11.9649	0.460002		
	1	s	3.66312	0.444594		
	2	s	0.539158	0.504860		
	2	s	0.167130	0.613125		
	3,4,5	x,y,z	4.18734	0.111922		
	3,4,5	x,y,z	0.854053	0.465078		
	3,4,5	x,y,z	0.199770	0.623756		
O	1	s	2331.57	0.0051237	−74.621447(^3P)	−74.80947
	1	s	350.640	0.0382146		
	1	s	79.5965	0.1712167		
	1	s	22.1200	0.4432487		
	1	s	6.82063	0.4824137		
	2	s	1.07057	0.4522493		
	2	s	0.321511	0.6081251		
	3,4,5	x,y,z	0.374851	0.6160137		
	3,4,5	x,y,z	1.68471	0.4751496		
	3,4,5	x,y,z	8.14220	0.1222798		

CALCULATIONS

Basis sets. — The *ab initio* computations were made with Clementi's IBMOL-6 program[9]. A minimal basis set of Gaussian functions, three 1s contracted to one 1s for hydrogen, and five 1s, two 2s, and three $2p_{xyz}$ contracted to one 1s, one 2s, and one $2p_{xyz}$ for carbon and oxygen, was used. The 96 electrons of glucose were thus described by 72 contracted functions and the 182 electrons of maltose by 137 contracted functions. The basis set is presented in Table I.

Integrals and SCF. — A threshold of 10^{-5} hartree was chosen both in the evaluation of integrals and in the energy difference of two consecutive iterations in the self-consistency process. On account of the small energy difference revealed by CFF computations between the two pairs of molecules, we had to use the double-precision version of the program. The total computational time amounted to ~8 h for one glucose and ~48 h for one maltose conformation on a UNIVAC 1100/20 system.

Usually, when doing conformational analysis by *ab initio* calculation, the molecular geometry is kept rigid and only torsional angles are changed. It is then possible to save a large part of the computational time by resorting to the SUB and ADD techniques[9], which allow one to compute only once those integrals that, in two or more conformations of a molecule, refer to atomic centres whose positions are not influenced by internal rotation. In the present case, this possibility could not be exploited, because energy minimisation with the CFF technique leads to a change of co-ordinates for all atoms. Therefore, the internal geometries of the pair of anomers and the pair of conformers show slight, but subtle, differences, which cannot be ignored if accurate comparisons are to be obtained.

Input geometries. — It was essential, for our purpose, to use exactly those conformations produced previously by our energy-minimisation program. The glucoses were minimised with a parameter set called[2] FF3, and later with a slightly simplified version[3] FF300, which was subsequently used for maltose.

The geometries chosen for the present study were the global minima of α- and β-D-glucopyranose, as obtained with FF300, and the two minima of lowest energy of β-maltose produced with FF300. The latter two correspond to minimum 1, with $(\phi,\psi) = (-21,-23)$, and minimum 2, with $(\phi,\psi) = (19,19)$[4].

RESULTS AND DISCUSSION

Absolute energies. — Energies and their components are given in Table II. The virial theorem is satisfied to 7×10^{-3}.

TABLE II

SCF ENERGIES AND COMPONENTS[a], IN HARTREE UNITS

	α-D-Glucopyranose	*β-D-Glucopyranose*	*Maltose 1*	*Maltose 2*
V_{nn}	829.02530	820.13036	2333.4855	2327.9436
V_{ne}	−3254.6045	−3236.6443	−7683.5252	−7671.6354
V_{coul}	1152.6010	1143.5365	2945.6991	2939.3580
V_{exch}	−83.91902	−83.91977	−159.00909	−159.00566
V	−1356.89723	−1356.89723	−2563.3496	−2563.3395
T	675.98565	675.98309	1277.2407	1277.2367
−V/T	2.0073	2.0073	2.0069	2.0069
E	−680.91158	−680.91414	−1286.10889	−1286.10284
E(C)	−225.65725		−451.31450	
E(O)	−447.72868		−820.83591	
E(H)	−5.96375		−10.93354	
E(atoms)	−679.34968		−1283.08396	
$E_{binding}$	−1.56190	−1.56446	−3.02493	−3.01888

[a] V, potential energy; T, kinetic energy; E, total energy; nn, nuclear repulsion; ne, nuclei–electron attraction; coul, coulomb integrals; and exch, exchange integrals.

Relative energies. — The energy difference between α- and β-D-glucopyranose is thus 0.00256 hartree = (6.721 ±0.003) kJ.mol^{-1}, with β-D-glucopyranose as the most stable configuration. The uncertainty in the difference is given as twice the difference in total energy between the two last iterations, which was almost the same for the two molecules. Our CFF results were 1.096 kJ.mol^{-1} with the parameter set FF3, and 1.283 kJ.mol^{-1} with FF300. The CFF calculations reproduce quite well the equilibrium ratio of glucose anomers in solution. The result obtained here gives an energy difference of the right sign. It should be stressed that the *ab initio* computations deal with completely isolated molecules, and that interactions with water are therefore not taken into account. This applies to CFF computations as well, but with the qualification that the force field is selected to reproduce conformations determined experimentally, though in this case not the anomer ratio, which simply came out with the correct value. Considering that the *ab initio* energy-difference amounts to only 4 × 10^{-6} of the total energy of either anomer, the agreement is appreciable. This result encouraged us to carry out the much more expensive calculations on maltose.

The energy difference between the two conformers of β-maltose is 0.00605 hartree = (15.879 ±0.004) kJ.mol^{-1}; this difference is 5 × 10^{-6} of the total energy of either conformer. With FF300, the value 2.371 kJ.mol^{-1} was obtained.

It is difficult to discuss the energies in comparison with earlier work, as very few papers treat molecules of comparable size with the same accuracy.

In 1969, Neely published an extended Hückel study of a few pyranoses[10], and found an energy difference of ~40 kJ.mol^{-1} between α- and β-D-glucopyranose in the $^4C_1$ conformation. He used standard bond-lengths and valence-angles, but did not list any torsional angles.

Askari *et al.* compared energy differences from *ab initio* and CFF calculations on substituted cyclohexanes[11] and decalones[12]; they used essentially the same approach as we have done, but with different programs. When comparing different conformers of the same molecules, they found the same qualitative energy-differences with the two methods; the quantitative differences agreed to within ~20 kJ.mol^{-1}.

Individual orbitals and energies. — Some noteworthy features are revealed by an inspection of the energies and eigenvectors of the molecular orbitals. For the sake of conciseness, we describe only minimum 1 of maltose, and follow the 91 occupied orbitals in the order of increasing energies. First, there are 11 orbitals with energies ranging from —20.582 to —20.534 hartree, which are almost pure 1s atomic orbitals of oxygen (contribution from these orbitals >98.9%); then a group of 12 orbitals ranging from —11.494 to —11.430 hartree, which are almost pure 1s atomic orbitals of carbon, either from a single or from two or three carbon atoms; then a group of 11 orbitals, ranging from —1.450 to —1.337 hartree, with predominant contribution from atomic 2s orbitals of oxygen; and a group of 12 orbitals, ranging from —1.116 to —0.819 hartree, with predominant contribution from 2s orbitals of carbon; and finally a group of 45 orbitals, with comparable contributions from very many atomic orbitals, the largest coming from 2p orbitals of oxygen or carbon. The energy of

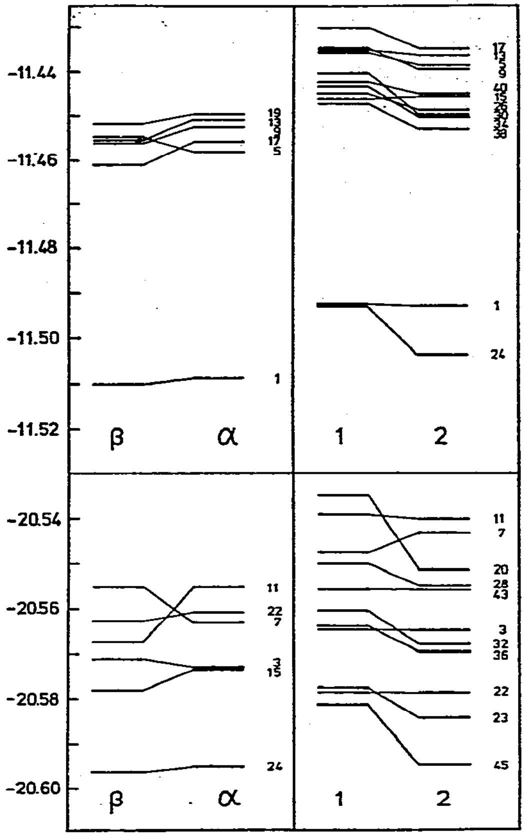

Fig. 3. Core energies of glucose (left) and maltose (right) in hartree. The core orbitals are almost pure C(1s) (upper) and O(1s) (lower) orbitals.

these orbitals ranges from —0.754 to —0.425 hartree, the last value pertaining to the so-called HOMO, the highest occupied molecular orbital.

The distributions of energies of the core orbitals of glucose and maltose are shown in Fig. 3. The three lowest-energy O(1s) orbitals correspond to O-24 of glucose and O-45, O-22, and O-23 of maltose, the ether oxygen atoms. Of the C(1s) orbitals, one of glucose and two of maltose are much deeper than the others, and correspond to the anomeric carbon atoms C-1 and C-24. The average energy-difference in 1s energy between the anomeric and the rest of the carbon atoms is almost the same for all four molecules. Any hydrogen contributes mostly to two types of molecular orbitals. One type is mainly built up from atomic 2p orbitals of the oxygen or carbon atom to which the hydrogen atom is directly bound; for instance, H-8(1s) mixes with O-7($2p_y$), H-10(1s) with C-9($2p_y$), H-12(1s) with O-11($2p_z$). The other type is formed from 2p orbitals of an oxygen or carbon atom at a distance of two or three bonds from the hydrogen; for instance, H-2(1s) mixes with O-22($2p_y$), H-6(1s) with O-11($2p_x$), and H-19(1s) with O-20($2p_x$).

The anomeric carbon atom. — With the simple potential-energy function employed in our previous work, we were unable to reproduce the shortening of the C–O bond from the anomeric carbon atom, the reason being our insistence on having only one type of carbon atom in the molecule. In spite of this, anomalies show up in the *ab initio* results, even though the anomeric C–O bond is too long[2,4] by 0.04 Å.

The anomeric carbon atom carries a positive net-charge, and its 1s orbital has a higher bonding-energy than a 1s orbital of any other carbon atom. As mentioned above and shown in Fig. 3, this chemical shift is almost constant for the molecules treated here. The energy differences between the centres of gravity of anomeric and all other C(1s) orbitals are, for α-D-glucopyranose, β-D-glucopyranose, β-maltose 1, and β-maltose 2: 0.055623, 0.054461, 0.052593, and 0.054066 hartree, or 1.514, 1.482, 1.431, and 1.471 eV, respectively. From this point of view, there is thus very little difference between the anomers α- and β-D-glucopyranose. For the maltose conformers, there is a striking difference. In minimum 1, the two anomeric carbon atoms C-1 and C-24 have electronically the same surroundings, judging from the 1s energy. In minimum 2, the binding energy of C-24 is much higher; the difference is 0.010447 hartree = 0.284 eV. It may be seen from the stereodrawings in Fig. 4 that, in minimum 2, the oxygen atom O-20 of the primary alcohol group is much closer to C-24 than it is in minimum 1, which must be the cause of the higher shielding. This is an example of the importance of interatomic relaxation[13] in a large molecule.

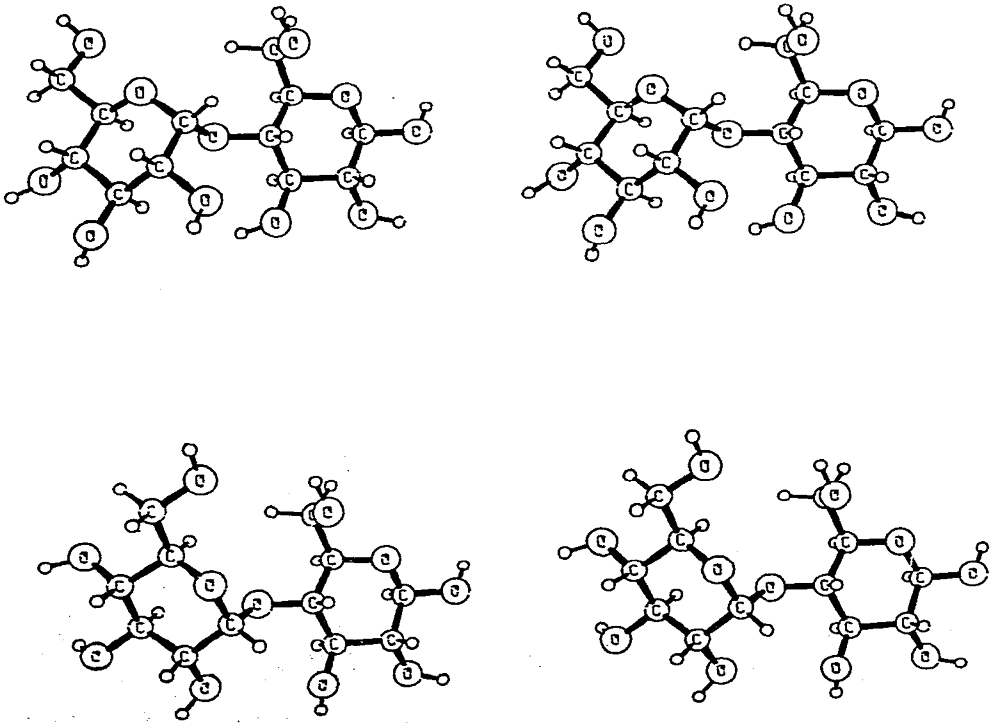

Fig. 4. Stereo drawings of β-maltose: minimum 1 (lower) and minimum 2 (upper).

Thus, a small conformational change, namely, rotation around the glycosidic bonds by 40° and 42°, produces an appreciable chemical-shift in the 1s energy. If it were possible to resolve a splitting of 0.28 eV on a C(1s) peak in an X-ray photoelectron spectrometer, structural information on individual conformers not obtainable by the n.m.r. method might be extracted for maltose and, by implication, for other disaccharides.

It should be possible to measure the C(1s) chemical-shift difference of 1.50 eV in glucose, and maybe use it for calibration purposes in measuring net charges of carbon atoms, if this is at all possible[13–15]. Such work would not be straightforward: suffice it to mention that we calculate a proportionality factor between chemical shift and net charge of 6.0, whereas Stucky *et al.*[14] found it to be 20.7, and Jolly and Perry[15], 30.5.

Dipole moments. — The following values, in debye, were calculated: α-D-glucopyranose, 2.74; β-D-glucopyranose, 4.64; β-maltose 1, 4.41; and β-maltose 2, 5.23.

Net charges and MOVS. — In the context of our study, two quantities are of particular interest, namely, the distribution of electronic charge on the atomic centres (Mulliken's electron-population analysis) and the partitioning of the total energy into pair-wise contributions (Clementi's bond-energy analysis).

The molecular orbital valency-state energy (MOVS) is the difference in energy between an atom in the molecule and the same atom in its isolated ground-state[1]. In Fig. 5 we present, using the total amount of data for the four molecules, a picture of MOVS plotted against net charge, which shows that each type of atom is clustered in two or three rather small regions of the plot. Such division into clusters serves as a

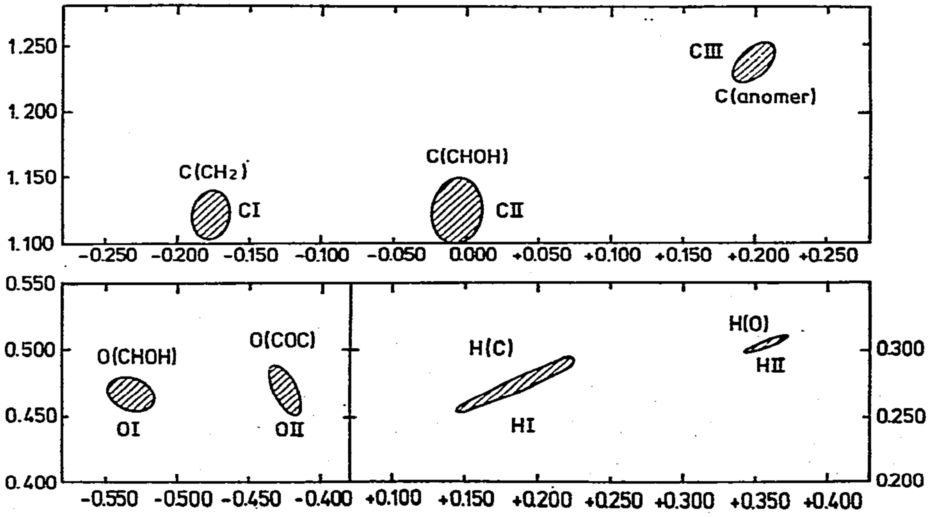

Fig. 5. Molecular orbital valency-state energies (MOVS) *versus* net charges for α- and β-D-glucopyranose and two conformers of β-maltose. Units are hartree *versus* elementary charge.

TABLE III

AVERAGE NET-CHARGES AND MOVS, IN UNITS OF ELEMENTARY CHARGES AND HARTREE

Atom	*Net charge*	*MOVS*	*Class*
$C(CH_2)$	−0.180	1.130	CI
C(CHOH)	−0.007	1.122	CII
C(anomeric)	+0.203	1.233	CIII
$C(CH_2 + CHOH)$	−0.042	1.123	
C(all)	−0.001	1.142	
O(CHOH)	−0.531	0.464	OI
O(COC)	−0.422	0.464	OII
O(all)	−0.506	0.464	
H(C)	+0.185	0.276	HI
H(O)	+0.360	0.306	HII
H(all)	+0.252	0.287	

basis for the assignment of any atom to a certain class of non-bonded interactions. This means that atoms in different classes will have different values of the parameters of non-bonded potential-energy functions. The classes in Fig. 5 are easily perceived: atoms fall into clusters according to the kind of atoms to which they are bonded. There is no difference in clustering between the four molecules, for instance, class I of carbon atoms contains C-19 of glucose and C-17 and C-40 of maltose, or carbon atoms bonded to C, O, H, and H.

Table III gives the average values of net charge and MOVS, and the classification of atoms. On the MOVS scale, there is no distinction between classes CI and CII, and OI and OII. For hydrogen, the spread within a class is almost as large as the distance between classes.

Bond-energy analysis. — The functional dependency of the energy of non-bonded interaction on distance can be derived from the off-diagonal terms of the BEA-matrix. The curves presented in Figs. 6–11 result from plots of these against non-bonded distances. For these plots, all data for 1,4- and higher interactions in minimum 1 of maltose were used. In regions where more information was desirable, in order to better define curves, additional data were taken from minimum 2 and from the glucoses. For the O---H case, 1,3-interactions were included, because of the lack of repulsion in 1,4- and higher interactions. In other cases, we checked that 1,3-interaction would fall on extensions of the curves shown.

Fig. 5 indicates that the O---O interactions should fall on three different curves. In spite of a rather large spread, it is possible to draw two curves; they are shown in Fig. 6. For OI---OI interactions, information is lacking for the range 3.3 to 4.2 Å, and the spread is large from 3.1 to 5.6 Å. For OI---OII interactions, information is lacking from 2.9 to 3.4 Å, and the spread is large from 3.4 to 4.4 Å. Only four points are available for OII---OII interactions; they indicate a third curve. Fig. 6 shows that Coulomb terms dominate beyond 3 Å.

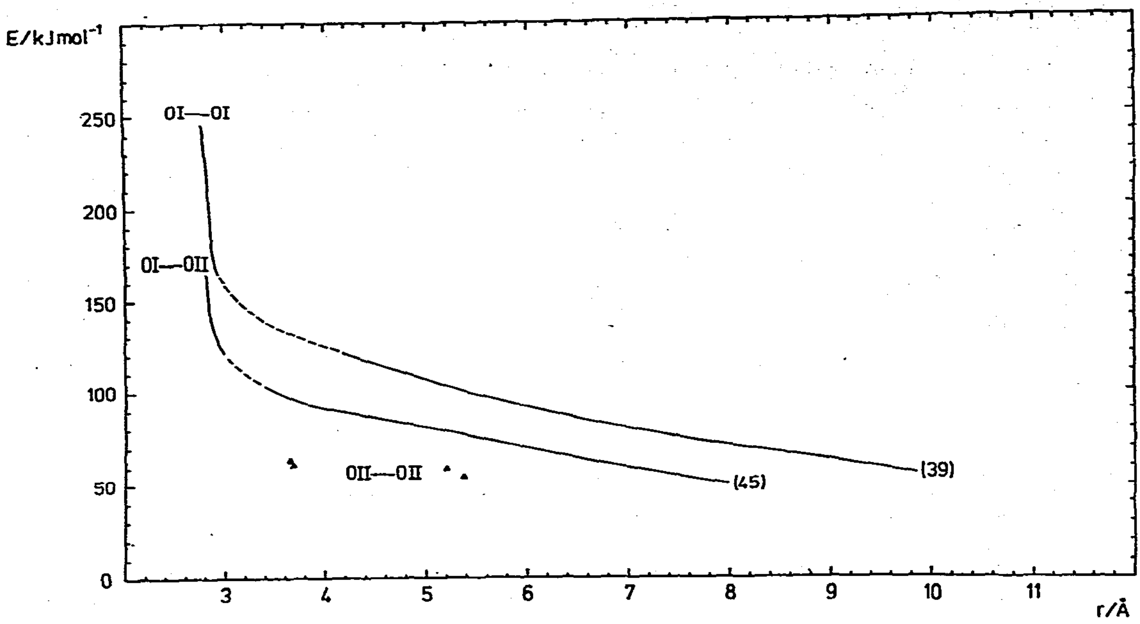

Fig. 6. Non-bonded interactions between oxygen atoms. Letters and roman numerals signify atom classes; arabic numerals in parentheses show numbers of points defining the curves.

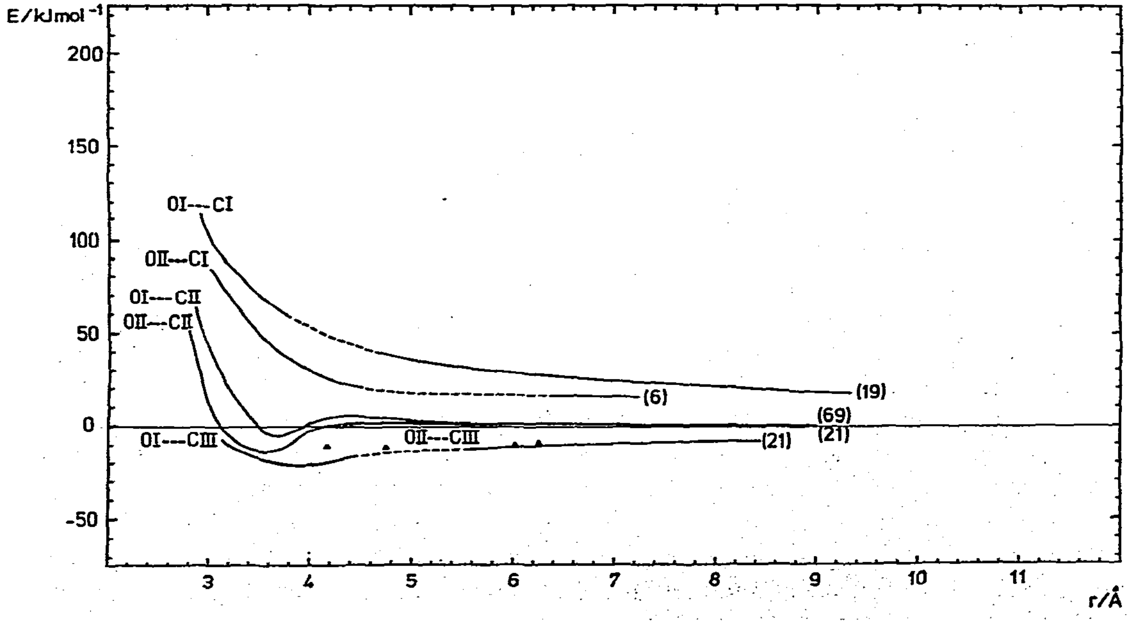

Fig. 7. Non-bonded interactions between oxygen and carbon atoms.

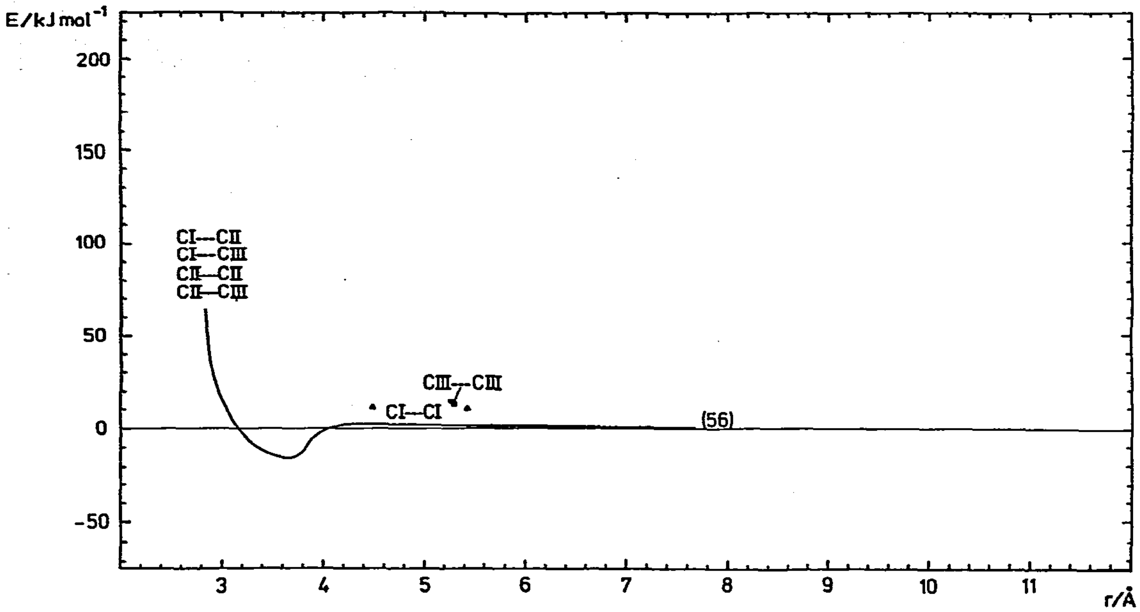

Fig. 8. Non-bonded interactions between carbon atoms.

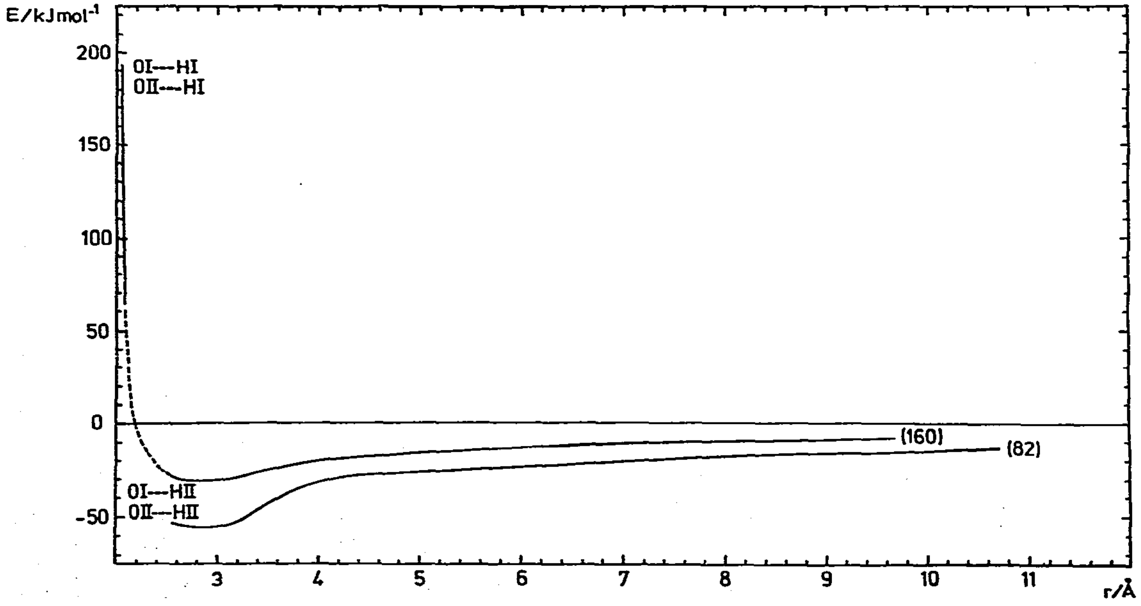

Fig. 9. Non-bonded interactions between oxygen and hydrogen atoms.

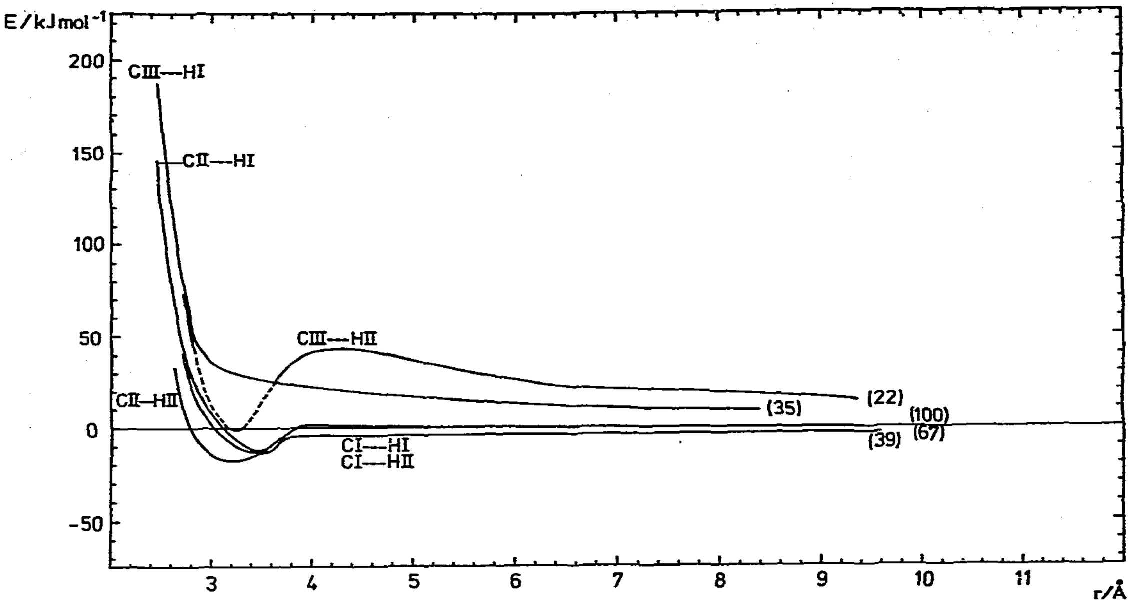

Fig. 10. Non-bonded interactions between carbon and hydrogen atoms.

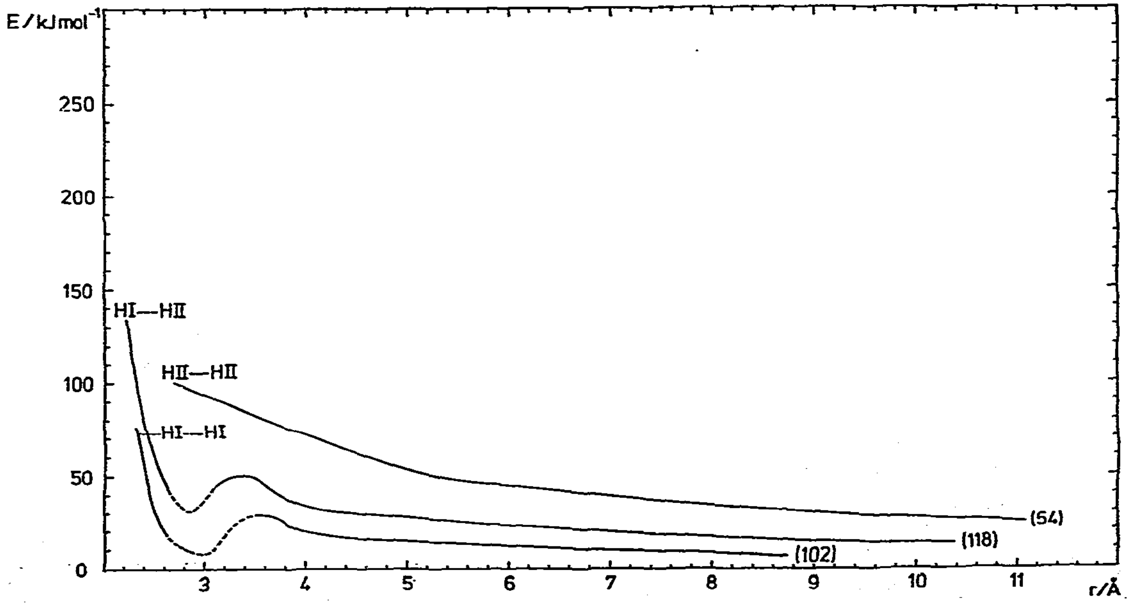

Fig. 11. Non-bonded interactions between hydrogen atoms.

For O---C interactions, six curves are indicated, but only five different curves can reasonably be drawn, as there are too few interactions between the anomeric carbon atom and ether oxygen, OII---CIII. They are given in Fig. 7; the four single-points show the OII---CIII interactions in the two maltoses. Intervals of missing data are indicated on the curves. The repulsive character of the two uppermost curves is due to the highly negative oxygen interacting with the negative carbon atoms of the primary alcohol groups. The two next curves have an increasing degree of van der Waals' appearance, because of the small negative charge on carbon which all but removes the Coulomb term. Interactions between oxygen and positively charged, anomeric carbon atoms are rather attractive.

According to Fig. 5, the C---C interactions should be represented by six different curves. Nevertheless, all carbon–carbon interactions involving class CII are well-described by only one curve, given in Fig. 8. From our entire material, only four points, corresponding to CI---CI and CIII---CIII, fall outside the curve, whereas CI---CIII interactions conform thereto. That only one curve suffices is due to the small net-charge of the secondary alcohol carbon atoms, which give rise to an imperceptible Coulomb contribution, making van der Waals' interaction the dominating energy-term at distances shorter than 4 Å.

For O---H interactions, four curves might be expected, but the data cluster neatly around two curves, one for OI---HI and OII---HI, and one for OI---HII and OII---HII, shown in Fig. 9. As expected, the O---HII curve shows a deep minimum corresponding to the hydrogen bond. The O---HI curve has been augmented with 1,3-interactions as mentioned above; this is not possible for the O---HII case.

The C---H interactions show a great deal of variability and complexity. Six curves might be expected; five can be found as shown in Fig. 10. CI---HI and CI---HII fall on one curve, of rather normal van der Waals' type. CII---HI and CII---HII fall on two similar curves, which coincide beyond 3.6 Å. CIII---HI is dominated by Coulomb repulsion due to the positive charge on the anomeric carbon atom. CIII---HII is similar at longer separations, but shows a quite unexpected and very deep minimum at 3.25 Å, due to the interactions between C-1 and H-8 in β-D-glucopyranose and between C-24 and H-29 in the maltoses. The analogous interactions between C-1 and H-8 in α-D-glucopyranose and in the maltoses are strongly repulsive, since they lie in an interval of distance of 2.7–2.8 Å.

For H---H interactions, the expected three repulsive curves are found; they are shown in Fig. 11. HII---HII is dominated by Coulomb repulsion, while the other curves show a rather deep van der Waals minimum. These two minima are not well-defined, due to a large spread. HI---HI and HI---HII have the same curious shape, showing both a maximum and a minimum. The explanation might be that van der Waals and Coulomb energies happen to have similar weight in a region where both have high curvature. A similar though not so pronounced behaviour is seen in most other plots.

CONCLUSIONS

We have shown that *ab initio* computations, even with a minimal basis set, give energy differences that agree semi-quantitatively with those found by purely empirical methods. Such computations are so costly that they should be undertaken only in exceptional cases, if the result wanted is just an energy value. They are more justified when essentially all extractable information can be put to use in different contexts.

An important outcome of these *ab initio* computations is the classification of atoms having the same atomic number into different classes, depending on the chemical environments of these atoms. In the empirical framework of consistent force-field calculations, the consequences of this classification should be tested in order to see whether significantly better results are obtained with an increased number of atom types, which implies an increased number of interaction parameters.

From the BEA curves, it may be concluded that a simulation of non-bonded interactions should consist of at least a van der Waals and a Coulomb energy-contribution. In cases where the Coulomb part dominates, the van der Waals part will be badly determined, but this will have no adverse consequences for energy calculations. Where the van der Waals part dominates, it is well-determined; the Coulomb part can be had from the population analysis. Where both have similar weights, the situation is one of a delicate balance, and the simulation may be very difficult. It is of over-riding importance to have a large number of points and therefore large and well-chosen molecules.

Work pertaining to simulation of the BEA curves and subsequent CFF calculations is currently in progress.

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