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An evaluation of the GLYCAM06 and MM3 force fields, and the PM3-D* molecular orbital method for modelling prototype carbohydrate–aromatic interactions

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ABSTRACT

The structures and interaction energies of 21 binary complexes of fucose and glucose with toluene, 3-methylindole or *p*-hydroxytoluene, evaluated at the DFT-D level, are used to judge the accuracy of the GLYCAM06 and MM3 force fields, and the PM3-D* molecular orbital method for modelling carbohydrate–arene interactions. The accuracy of the DFT-D method is substantiated by comparison with high level CCSD(T) calculations on a small number of representative complexes. It is found that a correct description of the intermolecular dispersive interactions is essential. Both the PM3-D* method and the GYLCAM06 force field yield interaction energies within 1 kcal mol^{-1} of the DFT-D values, whilst those from the MM3 force field are in error by more than 2 kcal mol^{-1}.

1. Introduction

Carbohydrate–protein interactions are important in a wide range of biological areas such as bacterial adhesions and toxins, viral glycoproteins, and in various amyloid-forming proteins such as those associated with Alzheimer's and Creutzfeldt's diseases [1–5]. Amino acids having aromatic side chains (tryptophan, tyrosine and phenylalanine) are frequently found in protein active sites which recognize carbohydrates, and the importance of the associated arene–carbohydrate interactions is well recognized [6–9]. A number of experimental [10,11] and theoretical [12–15] studies have shown that there are major contributions to these intermolecular interactions involving the aliphatic C–H and O–H groups which point towards the aromatic π system. The corresponding protein crystal structures display mainly C–H–π interactions, but in the binary complexes, fucose–toluene and α-methyl glucose-toluene, the most stable structures involve O–H–π interactions, which are reflected in their infrared spectra [11]. The contributions of dispersion forces to these interactions are extremely important, and both quantum mechanical and force field [16] approaches have been used to assess their magnitude.

The use of *ab initio* quantum mechanical methods to evaluate these dispersive interactions is particularly computationally intensive, and more cost effective approaches are generally employed. Density functional theory (DFT) is now an accepted route for accurately modelling most aspects of chemical structure and reactivity. Although commonly used density functionals such as BLYP and B3LYP generally fail to accurately describe such dispersive interactions [17,18], there are approaches based upon DFT methods which accurately model carbohydrate–arene interactions. Thus, of the new functionals developed by Truhlar and co-workers, the M06 family is particularly successful in describing short-range dispersive interactions [19], and has been applied to a range of carbohydrate–arene interactions [12].

An alternative strategy is to add an atom–atom pair-wise additive potential of the form C_6/R^6 to the DFT energy from a standard functional such as BLYP, in order to account for dispersion effects [17], and has been widely used to model π–π stacking, and other biologically important interactions [20]. Such an approach (DFT-D) is equally successful in modelling carbohydrate–arene interactions [13]. However, there is a need for more rapid methods for modelling these interactions, which can be applied to larger biologically important systems. This has traditionally been achieved *via* molecular mechanics (MM), with tailored force fields. An alternative approach, which has been shown to be applicable to a wide range of non-covalent interactions of biological importance, is to follow the philosophy of the DFT-D method, and to add a similar empirical dispersive term to the electronic energy calculated by a semi-empirical MO method such as PM3 or AM1 [21,22]. We have developed appropriate parameters for such models, the PM3-D* set being appropriate for carbohydrates [23]. We here assess the accuracy of this semi-empirical model, in predicting the structures and interaction energies of a number of carbohydrate–arene complexes.

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In view of the importance of an accurate treatment of non-covalent interactions in a range of biological situations, and the increasing use of quite sophisticated quantum mechanical methods that are being used for their description, there is considerable interest in the assessment of standard force field models against high quality *ab initio* treatments. Thus Sherrill et al. have studied a number of standard force fields, including AMBER and MM3, for the description of non-covalent interactions in a number of complexes containing benzene [24]. Spiwok et al. [16] have assessed a number of force fields for describing carbohydrate–aromatic interactions by comparison with MP2 calculations. Although the use of MP2 rather than higher level wavefunction methods was used in these 2006 computations, it is now generally recognized that MP2 interaction energies can be in error by up to $\sim 2\,\mathrm{kcal\,mol^{-1}}$ [25]. We here use interaction energies, computed by the DFT-D method to test MM3, as well the GLYCAM06 force field [26], which has been developed to treat carbohydrate systems, for describing these carbohydrate–arene complexes.

2. Computational details

2.1. Computational methods

The DFT-D [17,20] and PM3-D* [23] methods have been fully discussed previously. In brief, a pair-wise additive potential of the form C_6/R^6 is used to account for the long-range dispersion effects that are in general poorly described by semi-empirical methods and by common density functionals. The dispersion corrected total energy (E_{Total}) is then given by

$$E_{\mathrm{Total}} = E + E_{\mathrm{disp}} \tag{1}$$

where E is the normal self-consistent DFT or semi-empirical (PM3) energy and E_{disp} is an empirical term containing the dispersion correction:

$$E_{\mathrm{disp}} = -s_6 \sum_i \sum_{j>i} \left(\frac{C_6^{ij}}{R_{ij}^6} \right) f_{\mathrm{dmp}}(R_{ij}) \tag{2}$$

Here, the summation is over all atom pairs, $C^{ij}{}_6$ is the dispersion coefficient for the pair of atoms i and j (calculated from the atomic C_6 coefficients), s_6 is a scaling factor which is chosen to be 1.4 in line with the value used for the BLYP functional, and R_{ij} is the interatomic distance between atoms i and j. A damping function is used in order to avoid near singularities for small distances, given by

$$f_{\mathrm{dmp}}(R_{ij}) = \frac{1}{1 + e^{-\alpha(R_{ij}/R_0 - 1)}} \tag{3}$$

where R_0 is the sum of the atomic van der Waals radii and α is a parameter determining the steepness of the damping function. The atomic C_6 coefficients, and the R_0 and α values as well as the combination rule for the composite $C^{ij}{}_6$ coefficients are taken from the work of Grimme [17].

The PM3-D* semi-empirical method uses a modified version of the core–core repulsion function developed by Voityuk and Rosch [27], and the calculations reported herein were performed using our own local semi-empirical program [28]. The PM3-D* method was parameterized using the interaction energies of the complexes in the S22 database of weak complexes having the full range of important van der Waals interactions [29], together with 9 representative carbohydrate–benzene complexes calculated at the BLYP-D/TZV(2d,2p) level.

2.2. Model complexes

We have previously studied the fucose–toluene system at the DFT-D level [13] and have located ten minimum energy structures, **1**–**10**, which are close in energy, involving the three low energy conformers of fucose which differ in the orientation of O–H1 or O–H2, which in turn leads to different interactions with the π-system of toluene. These are shown in Fig. 1. In these structures, the aromatic group interacts with either the upper or the lower face of the sugar. The most stable group of complexes (**8**, **9**, **10**) involves the interaction of the arene with one O–H and one C–H group of the upper face of the sugar. The next group of complexes (**1**, **2**, **3**, **5**, and **6**) is higher in energy by 1–3 kcal mol^{-1}, and, except for (**3**), involve the interaction of only C–H groups of the lower face of the sugar. Complex (**3**) involves interactions of both one O–H and two C–H groups with the arene. Of the two remaining structures which are some 2 kcal mol^{-1} higher in energy, (**4**) involves an interaction with the lower face of the sugar, whilst (**7**) is the one structure which involves an interaction with the side of the sugar.

We have also studied 11 complexes of glucose with 3-methylindole and *p*-hydroxytoluene, which we have optimized at the DFT-D level, initial structures being based upon crystal structures of carbohydrate protein complexes, the PDB codes being 1KWF and 1GWM. There are six complexes (**11**–**16**) involving 3-methylindole, derived from the glucose–tryptophan structure, and five complexes (**17**–**21**) involving *p*-hydroxytoluene, derived from the glucose–phenylalanine structure. Most of these structures involve interactions with the lower face of the sugar, which is generally found in crystal structures. These structures again can be characterized in terms of the interaction of the C–H and O–H groups of the sugar with the aromatic ring. In addition there is the possibility of OH. . .N hydrogen bonding in the case of the indole systems. There are two structures (**11**, **12**) which show three CH–π interactions, two (**13**, **14**) which show one OH–π and one CH–π interaction, whilst (**15**) displays OH. . .N hydrogen bonding as well as having two CH–π interactions. The final glucose-3-methylindole complex (**16**) has a single OH-π as well as three CH–π interactions. The complexes of glucose with *p*-hydroxytoluene (**17**–**21**) have no OH–π interactions. OH–O hydrogen bonding is evident in (**19**, **20**), and (**17**) and (**21**) show 3 CH–π interactions.

2.3. Benchmark studies

In order to validate the DFT-D method for describing these aromatic–carbohydrate interactions we have reported *ab initio* benchmark studies of some representative complexes. Briefly, the MP2 energies of the complex and monomers are extrapolated to the basis set limit by the use of the aug-cc-pVDZ and aug-cc-pVTZ basis sets to give the MP2/CBS energy. This value is then corrected for higher order correlation effects obtained by computing MP2 and CCSD(T) energies using a modified 6-31G** basis followed by employing the difference between these energies to obtain the correction. Basis set superposition errors (BSSE) are also taken into account in the calculation of the interaction energies [29]. However, recently Takatani et al. [30] have studied the S22 test set of non-covalent complexes, and find that the basis sets used to compute the CCSD(T) interaction energies are insufficient for some complexes, and can lead to errors of up to 0.6 kcal mol^{-1} in the interaction energies, although the error is usually considerably smaller than this value. We have previously found that the unsigned mean error in the interaction energies given by the DFT-D method for the S22 training set was 0.72 kcal mol^{-1} [20], which is only changed to 0.68 kcal mol^{-1} when the modified S22 test set (S22A) is employed. We thus believe that our *ab initio* benchmark set is adequate to assess the accuracy of the DFT-D method.

The complexes previously studied in this way were firstly structures (**5**) and (**8**), involving the interaction of toluene with the lower and upper faces respectively of fucose. Structure (**5**) has three C–H–π interactions, whilst structure (**8**) has one C–H–π and one O–H–π interaction. In addition we have studied the

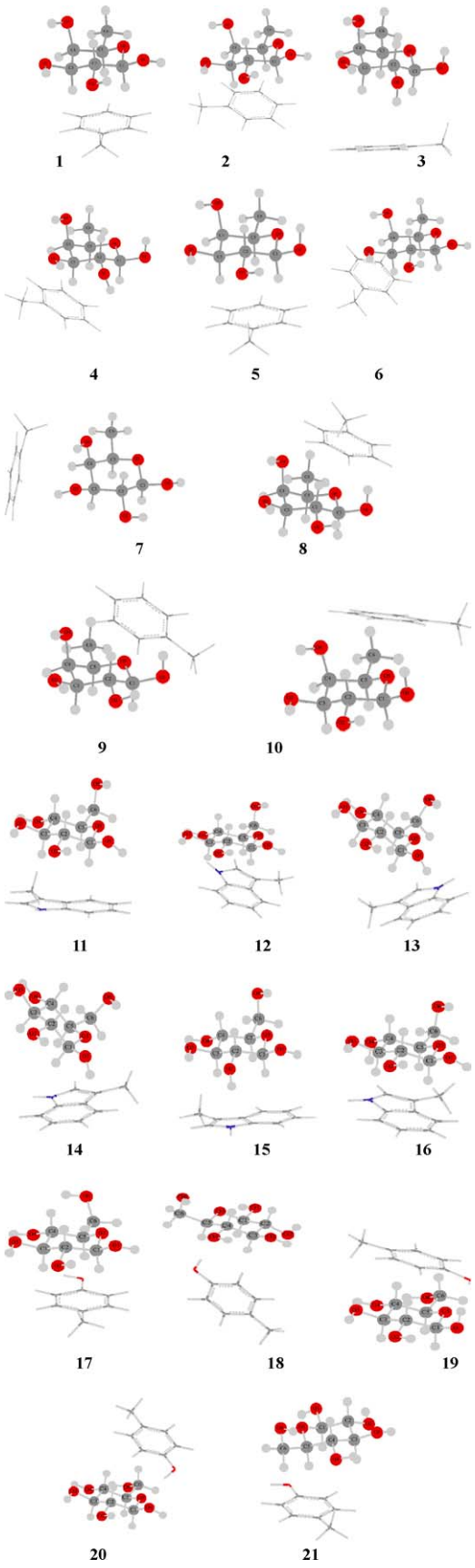

Fig. 1. Optimized structures (DFT-D), of fucose–toluene (**1**–**10**), glucose-3-methylindole (**11**–**16**), and glucose-*p*-hydroxytoluene (**17**–**21**).

Table 1
Interaction energies (kcal mol^{-1}) of benchmark complexes.

Structure	Complex	CCSD(T)	DFT-D
Fucose–toluene	**5**	−6.81	−6.52
Fucose–toluene	**8**	−9.21	−9.28
Glucose-3-methylindole	**14**	−10.55	−10.33
Glucose-*p*-hydoxytoluene	**17**	−7.42	−7.30
MUE			0.18

p-hydroxytoluene–glucose complex, structure (**17**), having three C–H–π interactions. To ensure that complexes involving tryptophan were also accurately treated by the DFT-D method we have calculated the interaction energy of the glucose–tryptophan complex (**14**) by this high level *ab initio* scheme. This gave an interaction energy of 10.55 kcal mol^{-1} to be compared to the DFT-D values of 10.33 kcal mol^{-1}. Thus, for a representative family of carbohydrate–aromatic complexes, the DFT-D method gives a mean unsigned error (MUE) of 0.18 kcal mol^{-1} when compared to the benchmark *ab initio* results (Table 1), which is well within the error expected for the *ab initio* data. We are thus confident that we can employ the DFT-D results to judge the accuracy of the range of less computationally demanding methods tested herein.

We have optimized the structures and computed the interaction energies of this set of 21 carbohydrate–arene complexes, employing both the quantum mechanical semi-empirical PM3-D* method and two force fields. The first is the widely used MM3 and the second is the biomolecular force field GLYCAM06, as implemented in AMBER09 [31]. Here the atomic charges for toluene, 3-methylindole and *p*-hydroxytoluene were derived by the RESP method at the HF/6-31G* level.

3. Results and discussion

In Table 2 we compare the interaction energies, and in Table 3 the structures of the complexes characterised by the distance between the centre of mass of the carbohydrate and that of the arene calculated herein, with those from the DFT-D method previously reported.

We consider first the results from the PM3-D* method. The interaction energies (Table 2) computed for the PM3-D* structures are close to the DFT-D values, with a MUE of 0.62 kcal mol^{-1}. Optimization of the structures increases the MUE somewhat to 1.02 kcal mol^{-1}, with the MUE for the intermolecular distance being 0.16 Å (Table 3), values which are certainly within the error bounds of the DFT-D calculations. However, we do note that a number of the initial DFT-D structures have collapsed to a common structure. Thus, the three initial fucose–toluene structures, (**1**, **3**, **5**) which involve CH–π interaction with the lowest face of the sugar have collapsed to one structure, as have structures (**2**, **4**, **6**) which also involve these interactions. Similarly, structures (**9**, **10**), which involve one OH–π and one CH–π with the upper face of the sugar collapse to a common structure. However, in line with the DFT-D predictions, the most stable group of complexes (**8**, **9**) have both O–H and C–H interactions with the lower face of the sugar, the complexes (**1**, **2**, **6**) which have only C–H interactions with the sugar, being to slightly higher energy. No such collapse was found for the model glucose–tryptophan or glucose–tyrosine interactions.

Turning now to the force field calculations, we find that for the DFT-D structures the interaction energies for the GLYCAM06 force field are considerably better than the MM3 values, with MUE values of 0.79 and 3.33 kcal mol^{-1} respectively. There is a similar trend in the interaction energies and inter-ring separations of the corresponding optimized structures. The MM3 force field gives MUE values of 0.33 Å and 2.30 kcal mol^{-1}, which are considerably worse than those given by the PM3-D* method. However, the

Table 2
Interaction energies (kcal mol^{-1}) of model complexes. The values in parentheses for the DFT-D and PM3-D* methods, are the dispersive energy contributions. The structures are optimized for the various methods (opt) where stated; otherwise the optimal DFT-D structures are used. The values from the GLYCAM06 force field are labelled GLY06. The MUEs are with respect to the DFT-D values.

	Complex	DFT-D (opt)	PM3-D*	PM3-D* (opt)	GLY06	GLY06 (opt)	MM3	MM3 (opt)
Fucose–toluene	**1**	−6.25 (−8.51)	−6.92	−6.79 (−9.38)	−6.56	−6.59	−3.64	−4.13
	2	−6.18 (−8.63)	−6.85	−6.51 (−9.26)	−6.40	−6.54	−3.48	−4.10
	3	−8.11(−7.46)	−7.93	−6.79 (−9.38)	−9.11	−9.37	−6.30	−7.73
	4	−6.19 (−8.60)	−6.83	−6.51 (−9.27)	−6.38	−6.54	−3.55	−4.08
	5	−6.52 (−8.60)	−7.03	−6.79 (−9.39)	−6.54	−6.59	−3.55	−4.08
	6	−5.92(−8.00)	−6.00	−6.51 (−9.28)	−5.64	−6.58	−3.00	−4.13
	7	−7.79 (−7.21)	−6.78	−6.64 (−9.12)	−7.75	−6.35	−6.25	−5.32
	8	−9.28 (−8.92)	−8.94	−7.50 (−9.51)	−9.56	−9.42	−6.25	−7.73
	9	−7.84 (−8.01)	−7.27	−6.95 (−9.09)	−8.27	−5.82	−6.15	−7.33
	10	−7.58 (−6.88)	−7.29	−6.95 (−9.08)	−8.49	−8.80	−6.25	−7.73
Glucose-3-methylindole	**11**	−9.78 (−10.6)	−9.83	−10.12 (−11.0)	−10.06	−10.60	−4.86	−5.29
	12	−10.55 (−9.1)	−10.52	−9.31 (−9.9)	−11.32	−12.20	−5.17	−5.23
	13	−10.20 (−9.5)	−10.83	−9.43 (−11.2)	−11.03	−11.35	−6.60	−8.23
	14	−10.33 (−10.2)	−10.47	−9.25 (−11.3)	−11.17	−11.66	−6.40	−8.37
	15	−11.46 (−11.0)	−12.16	−8.89 (−10.7)	−13.19	−13.15	−7.34	−8.46
	16	−9.96 (−10.0)	−11.88	−12.12 (−12.8)	−12.77	−13.55	−6.75	−7.99
Glucose-*p*-hydroxytoluene	**17**	−7.27 (−9.2)	−8.10	−9.19 (−10.2)	−7.98	−10.11	−3.91	−4.33
	18	−10.56 (−6.2)	−9.57	−8.22 (−5.9)	−8.06	−9.88	−0.56	−5.83
	19	−9.77 (−9.0)	−8.44	−8.68 (−11.2)	−10.62	−10.02	−7.41	−8.00
	20	−9.04 (−8.4)	−9.88	−8.93 (−11.5)	−8.37	−10.02	−6.45	−7.25
	21	−7.16 (−8.6)	−7.81	−7.17 (−10.1)	−8.18	−7.72	−3.93	−4.32
MUE			0.62	1.02	0.79	1.11	3.33	2.30

GLYCAM06 force field is a considerable improvement over MM3, with MUE values of 0.16 Å and 1.11 kcal mol^{-1}. As in the PM3-D* calculations, we found in these force field calculations that a number of structures collapsed to a single minimum energy structure. Thus, in the MM3 calculations, the groups of structures (**1**, **6**) and (**3**, **8**, **10**) each collapsed to a single structure. In the GLYCAM06 studies, a collapse of structures (**1**, **5**), (**2**, **4**) and (**19**, **20**) was found. In all these groups of structures, except one, their collapse to a single structure is clearly feasible. However, structures (**3**) and (**8**) involve interactions with different faces of the carbohydrate, and here there was considerable motion of structure (**3**) to achieve the more stable conformation found in structure (**8**).

In an attempt to explore further the reasons for the differing success of the two force fields used here, we have examined the various contributions of the different interactions to the overall interaction energy, bearing in mind that it is the overall accuracy which is important, rather than the perceived accuracy of a particular component. In the case of the PM3-D* calculations, the dispersive contribution is readily identified, and we have thus focused on this contribution to the different models. We find that for the dispersive energy, the MUE between the PM3-D* values and those given by the two force fields are 0.9 and 2.2 kcal mol^{-1} respectively for the GLYCAM06 and MM3 force fields. We note that the overall MUE values for these two force fields differ by ∼1 kcal mol^{-1} so that it is tempting to ascribe the superior per-

Table 3
Distance (Å) between centre of mass of carbohydrate and arene in the model complexes. The values from the GLYCAM06 force field are labelled GLY06.

	Complex	DFT-D	PM3-D*	GLY06	MM3
Fucose–toluene	**1**	4.21	4.18	4.20	4.38
	2	4.37	4.34	4.42	4.54
	3	4.44	4.18	4.37	4.30
	4	4.37	4.34	4.42	4.55
	5	4.20	4.18	4.20	4.38
	6	4.58	4.34	4.41	4.38
	7	5.02	4.41	5.27	5.36
	8	3.95	3.93	4.17	4.30
	9	4.26	4.24	4.18	4.58
	10	4.53	4.24	4.56	4.30
Glucose-3-methylindole	**11**	4.11	4.32	4.13	4.35
	12	4.43	4.38	4.56	5.10
	13	4.46	4.37	4.51	4.82
	14	4.44	4.40	4.58	4.88
	15	4.17	4.29	4.17	4.61
	16	4.20	4.04	4.17	5.07
Glucose-hydroxytoluene	**17**	4.11	4.05	4.50	4.33
	18	5.42	5.59	4.72	4.77
	19	4.06	3.89	3.83	4.09
	20	4.39	3.84	3.83	4.94
	21	4.15	4.04	4.10	4.43
MUE			0.16	0.16	0.33

formance of GLYCAM06 to a better description of the dispersive interactions.

4. Conclusions

In this short paper we have examined the use of a semi-empirical MO scheme (PM3-D*) and two different force fields to predict the structure and interaction energies of a family of carbohydrate–arene complexes which are typical of the non-bonded structures encountered in carbohydrate–protein complexes. As we have previously found for a range of non-covalent complexes, important in both biological systems [20] and in materials chemistry [32], the dispersive interactions are critical to the recognition process. Indeed, in most of the complexes studied herein, the interactions are repulsive in the absence of the dispersive forces.

We find that the computationally efficient PM3-D* method predicts structures and energies which are only slightly inferior to those from the more computationally demanding DFT-D method. However, the GLYCAM06 force field is of similar accuracy to the PM3-D* method, whilst the MM3 force field is definitely inferior. It is likely that a more appropriate description of the dispersive interactions is responsible for the success of the GLYCAM06 force field. Thus, this force field is the preferred rapid computational method to study carbohydrate–aromatic interactions, particularly when a large number of structures need to be considered, such as in MD simulations.

Recently, Sherrill et al. [24] have assessed the use of a number of standard force fields, including AMBER and MM3, for the description of non-covalent interactions in the benzene dimer, and the benzene–CH_4 and benzene–H_2S complexes, and find that all are semi-quantitatively correct, but none is consistently reliable. Our conclusions on the use of the AMBER force field would appear somewhat more optimistic than those of Sherrill et al.

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