Computational Studies of Binding Energies and Structures of Methylamine on Functionalized Activated Carbon Surfaces

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Abstract

Empirical force fields and density functional theory (DFT) were used to study the binding energies and structures of methylamine on the surface of activated carbon (ACs). This is a first step in studying the adsorption of alkyl amines on the surface of functionalized ACs. The force fields used were Dreiding (DFF), Universal (UFF) and Compass (CFF) models. The generalized gradient approximation with Perdew Wang 91 (PW91) functional was used for DFT calculations. In addition to obtaining the amine-carboxylic acid adsorption energies, the results were used to establish reliability of the empirical models for these systems. CFF predicted a binding energy of (-9.227 kcal/mol) which agreed with PW91 at (-13.17 kcal/mol), compared to DFF (0 kcal/mol) and UFF (-0.72 kcal/mol). However, the CFF binding energies for the amine to ester and ketone disagreed with PW91 results. The structures obtained from all models agreed with PW91 results.

Key words: *Activated Carbon, Amine, Binding energy, DFT, Force fields.*

1. Introduction

Activated carbons (ACs) have been used extensively in the removal of waste water contaminants because of their high availability, high surface activity and chemical stability. [1,2,3]. It is also known that the surface activity of ACs is enhanced by the presence of polar functional groups such as C=O, O-H, and C–O. [4,5]. Depending on the pH, protons may be adsorbed or removed from these surface groups, hence leading to a surface charge. The charge on the surface plays a dominant role in the adsorption of the waste water contaminants. The removal efficiency is also influenced by other factors, such as solution concentration, solution ionic strength, and the adsorbent modification procedure [6]. Nonetheless, the explanations of the interaction between the π electrons of the aromatic structure, metal ions and the intermediate ligand that sustain an adsorption process remain uncertain. The scarcity of this information is further worsened by the variety in pore structure and surface chemistry for each functional group.

AC adsorbents are also used industrially in the recovery and purification of gold, in the form of cyanide complexes, using the Carbon-in-liquid process. There are continuous investigations in this area of research [8, 9, 10]. In addition, Ralph *et al*. [11] used polymer powders, membranes and coated fabrics like nylon to recover platinum from solutions containing $[PtCl_6]^{2-}$. For effective removal of the metal, the process was enhanced with further dissolution of the adsorbents in *aqua regia*.

Some researchers have focused on functionalizing ACs in order to induce certain desired properties, such as enhancing surface acidity and basicity, in order to attract transition metal ions. For example, platinum group metals adsorbed on modified carbon are easier to remove than when they are adsorbed on native carbon. [12,13]. The first report on the usage of organic ligands such as amines in the form of tris-hydroxymethane, thio and dithio phosphoric acid groups on the surface of ACs to induce selectivity towards platinum, rhodium and palladium metal complexes was by Kasaini *et al.* [14]. In their research, the efficacy of amine treated ACs was studied in batch adsorption tests. They concluded that amine-treated ACs exhibited an affinity for platinum ions while thiophosphate-treated activated carbons showed an affinity for palladium ions in chloride media. However rhodium complex ions were not adsorbed by the chemically treated ACs.

Yantasee *et al*. [15] also concurred that adsorbent containing nitrogen groups would enhance metal ion adsorption through surface chelation mechanisms, although this was with reference to lead (Pb) ion adsorption. Later, the concept was used by Fujiwara *et al*. [16] and their findings identify nitrogen sites as the main adsorption sites for Pd, Pt, and Au. Recently, Kasaini *et al.* [17] used amine treated ACs (Norit 0.8) at a pH of 2 to adsorb Pt ions contained in a mixture of Pt and base metals in chloride solution. Their results ascertained that amine treated ACs adsorb Pt ions better than native ACs, and in addition establishing the minimum amine dosage for effective uptake of Pt and Pd.

Computational methods have become an important tool in providing data of atomic and molecular clusters that give valuable insight into the mechanisms of molecule surface binding and the structures of the adsorption complexes. Calculations based on density functional theory (DFT) and empirical force fields have been used successfully in the

prediction of gas solid interactions and the calculation of binding energies on the surfaces of carbon based adsorbents [18, 19]. In 2004 Miyamoto [20] performed a comparative study of DFT and quantum chemical molecular dynamics for cyclo-propane adsorption onto copper surfaces. The adsorption energies obtained were comparable to experimental data and the structural properties obtained from quantum molecular dynamics calculations were consistent with those obtained from DFT methods. Künzel [21] used a combination of DFT and empirical force fields to study graphite surface template structures of *bis*-(terpyridine) derivatives. The authors assessed, among others, the suitability of each force field (DFF, UFF and CFF) in interpreting geometric parameters, and structural conformities of these derivatives. They concluded that geometric parameters were described adequately by all force fields. However, there was a discrepancy in the calculated torsion angles. The CFF gave the best adsorption energies of the three empirical force fields.

Similar computational methods to those used by Künzel [21] are used in this contribution to study the adsorption of methylamine (CH_3NH_2) on benzocarboxylic acid (C_6H_5COOH). This is an initial step towards studying the adsorption of amines on several activated carbon (AC) functional groups, which has been used in the experiments of Kasaini *et al.* [7, 13, 14]. In these experiments the amine groups were adsorbed onto the AC surface at pH 10, where surface charge was slightly negative and constant, before a Pt metal ion solution at pH 2 was introduced to the system. Here we focus on the first step, i.e., adsorption of amines on the AC, wherein the ACs simulated corresponds to the surface charge attained by native ACs when they are in a solution at pH 10, with the future aim of extending this work to the adsorption of Pt ions on the amine-treated surface. This work therefore serves as a preliminary step in the development of a carbon based adsorbent, tailor-made for the separation of platinum group metals found in low concentrations of 50 ppm and below, found in waste water and barren solutions from mining effluents.

In the present contribution we focus on methylamine (CH_3NH_2) adsorbed on benzocarboxylic acid (C_6H_5COOH). This system is used to model the experimental situation where amines, usually with 4 carbon entities, are adsorbed on functionalized AC. It is a sufficiently small system to allow for accurate DFT calculations, while at the same time it is expected to yield qualitatively correct chemistry. We focus on the carboxylic acid functional group since our calculations indicate that this group yields the largest binding energy to the amine, as compared to ether, ketone, ester and C=C groups. Some results from the ketone and ester groups, which have larger binding energies than the ether and C=C groups, are also given. The CH_3NH_2 and C_6H_5COOH molecules are neutral in these calculations since this is the simplest system to test the validity of the empirical force fields studied here. The importance of positively charged surfaces, which is more important at the low PHs when the Pt ions are introduced to the surface-modified AC, will be addressed in future work. The empirical force fields used in this work are the same as those used by Künzel [21] (i.e. DFF; UFF and CFF) and the generalized gradient approximation (GGA) with the Perdew Wang 91 (PW91) functional was used for the DFT calculations. The aim of the study is two-fold: First to obtain the chemical structure and binding energy for the $CH_3NH_2 - C_6H_5COOH$, which is expected to be typical for the more general amine-carboxylic acid AC surface and, second to determine which, if any, of the empirical force fields provides a valid description of these

systems. The results obtained in these studies forms the base for future studies focusing on the effect of hydration on the adsorption structures and energies, as well as the adsorption of platinum ions in chloride media [$PtCl_6^{2}$, $PtCl4^{2-}$ and $PdCl2^{2-}$] to the functionalized AC surface.

2. Models and Methods

The three empirical force fields used in this study are the same as those used in previous studies of molecular adsorption on graphite [21]. They are the Compass (CFF), Dreiding (DFF) and Universal (UFF) force fields as implemented in the Materials Studio® software package [22]. The CFF has been optimized to both ab initio and empirical data for condensed phase applications and has been widely used in simulations of liquids, crystals, and polymers, including some transitional metals such as Cr ,Ni ,Pd ,Pt etc. [23]. The DFF is commonly used in the prediction of structures and dynamics studies of organic, main group inorganic and biological systems. Its functional form is detailed in reference [24]. The UFF is based on bond hybridization and connectivity, and is thus applicable to all elements in the periodic table [25]. Although the use of force fields in studying complex surface structures and mechanical properties is still not common, their application in polymer, composite materials and protein research has advanced [26, 27, 28].

In this work density functional theory (DFT) was used to obtain more accurate results for the CH_3-NH_2 – C_6H_5COOH binding energy and structure and to assess the validity of the three empirical force fields. DFT was chosen for this study since it yields accurate atomic energies and reaction barriers for molecular systems [29] in a computationally tractable time, which is not the case for post Hartree-Fock methods that give similar accuracy. In this work the calculations were based on the generalized gradient approximation (GGA) [30] parameterized by Perdew Wang 91 functional (PW91) [31], which is known to yield good prediction of Van der Waals interactions in organic and hydrogen bonded systems [32, 33].

As discussed above, the activated carbon (AC) was represented by a single benzene ring, functionalized with either carboxylic acid, ester, ketone, ether or C=C groups. This is illustrated for ester and ketone groups in Figure 1. This model was chosen since it is the simplest molecule that includes the functional group and the aromatic ring that is expected to be found in the AC. Preliminary calculations done in our group indicate that the carboxylic acid group shows the largest binding energy to the amine, and hence we focus on this functional group in this contribution. Comparison was made with some results obtained for the ester and ketone groups, which have larger binding energies than the ether and C=C groups. The amine was modeled by the CH_3-NH_2 molecule.
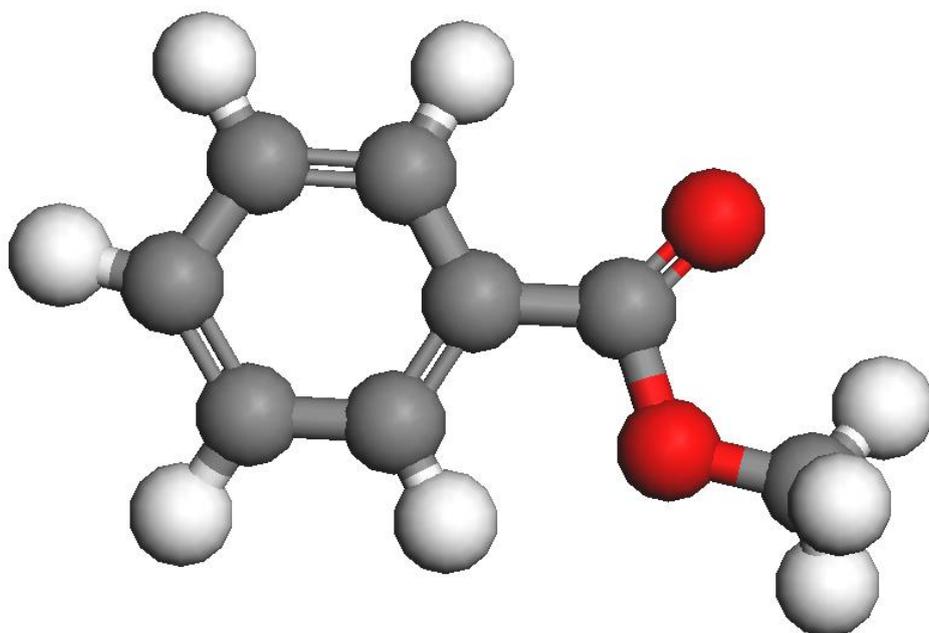
a) Activated Carbon functionalized with an Ester group
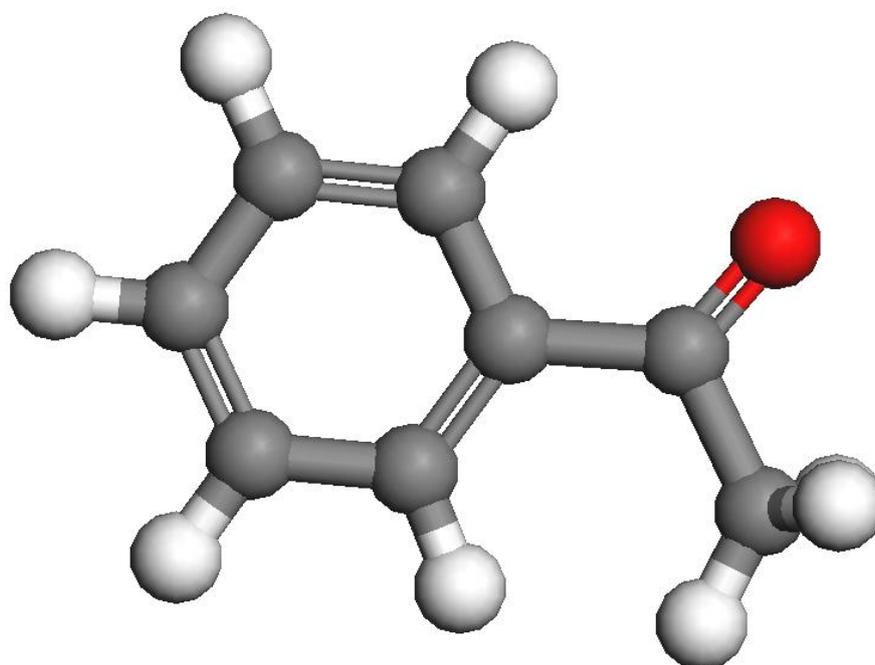
b) AC functionalized with a ketone group.

Figure 1. Structures used to model the ester (a) and ketone (b) functionalized AC. The structures were obtained by annealing using the CFF and then geometry optimization with PW91.

Minimum energy geometries for the CH_3-NH_2 and C_6H_5COOH molecules as well as the $CH_3NH_2 - C_6H_5COOH$ complex were obtained for each of the three force fields by first performing a geometry optimization and then a simulated annealing (i.e., nine minimum energy geometries were obtained). The simulated annealing was performed in an attempt to locate a chemically relevant or global minimum. Each molecule and complex was annealed over 50 cycles at an initial temperature of 300 K and a mid-cycle temperature of 500 K. This temperature range was chosen since it allowed the molecule/complex to transverse energy barriers while, at the same time, not allowing dissociation. Geometry optimization was done between each cycle, and the minimum energy configuration was the structure with the lowest energy.

The nine minimum energy structures obtained from the simulated annealing (three structure for each force field) were used as input coordinates for the PW91 calculations. In principle, this is not necessary if two of the force fields yielded the same structure, but all nine calculations were performed here to ensure completeness. The first Brillouine zone was sampled using Monkhorst–Pack technique. For this non metallic system, fine meshes of 2 x 2 x 2 k-points were generated in a non periodic super cell of 30 x 30 x 30 Å. The cell size was set so that subsequent computations involving water and Pt ions can be done without changing the cell size (platinum chloride complexes require larger cell dimensions).

The results of the PW91 geometry optimizations were used as follows: First, the energies for any given structure (e.g., the amine) that were obtained when using input from the three different force fields was compared. The force field that gave the structure that yielded the lowest energy gives the best description of the molecule/complex, provided the PW91 optimization does not significantly change the input geometry. Second, the binding energy was calculated from Chi et al. [34]:

$$E_{binding} = E_{complex} - [E_{AC, fg} + E_{amine}] \qquad (1)$$

$E_{complex}$ is the energy for functionalized AC bound to the amine, e.g., for the $CH_3NH_2 - C_6H_5COOH$ complex shown in Figure 2. $E_{AC, fg}$ is the minimum energy of the functionalized AC model, e.g., C_6H_5COOH, and E_{amine} is for the amine group. The binding energy calculated from the PW91 method (after optimization from the inputs obtained from the three different force fields) was compared to the energies calculated directly from the corresponding force field. A good agreement between the binding energies obtained from the force fields and the DFT calculations indicates that the force fields provide a valid description for that system.
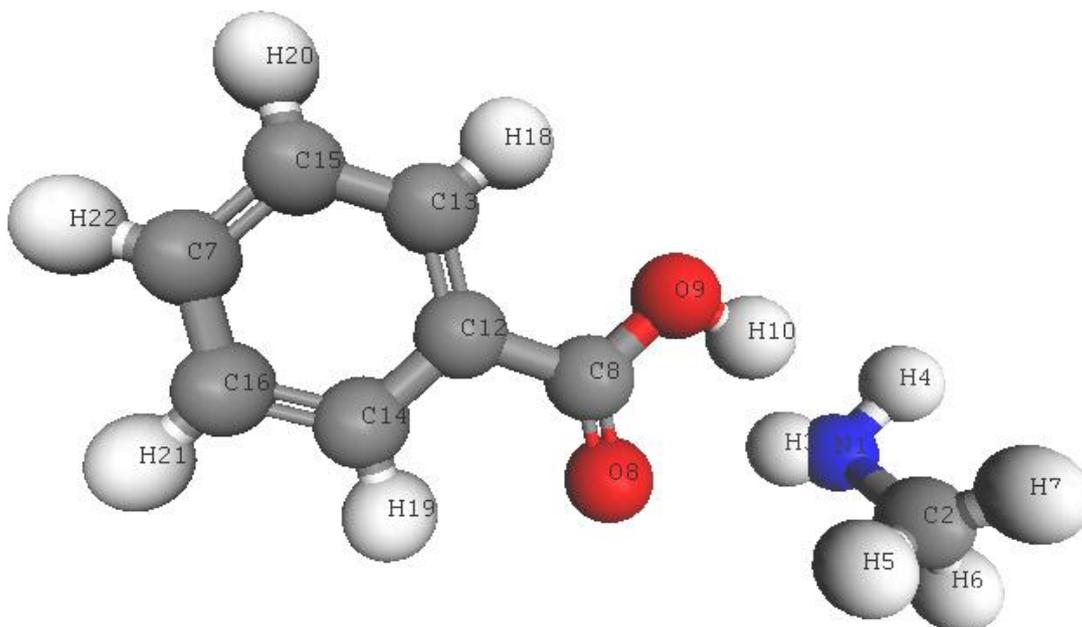
Figure 2: Structure used to model the carboxylic acid functionalized AC – amine complex. The structure was obtained by annealing using the CFF and then geometry optimization with PW91.

3. Results and Discussions

3.1. Methylamine (CH₃NH₂)

A typical structure for the CH_3NH_2 molecule is shown in figure 3 .The figure also shows the labels used in Table 1. . It must be noted that the literature data is not specific for the CH_3NH_2 molecule but are general for all amines. Hence, only qualitative comparison can be made with these values.
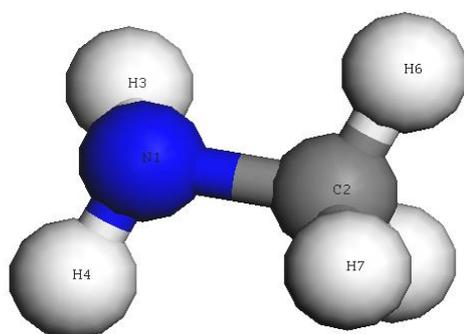

Figure 3: Structure used to model methylamine. The structure was obtained by annealing using CFF and then followed by geometry optimization with PW91.

Table 1: Selected bond lengths, bond angles and torsion angle obtained after PW91 relaxation when the initial geometry was obtained from CFF, DFF, and UFF. The values obtained from force field calculations are shown in parenthesis. Literature values [35] are also given.

Functional group	Force fields			
Amine	Compass	Dreiding	Universal	Literature
Bond length [Å]				
N_1C_2	1.467 **(1.550)**	1.464 **(1.453)**	1.464 **(1.456)**	1.47
N_1H_4	1.014 **(1.003)**	1.013 **(1.101)**	1.013 (**1.046**)	1.01
$N_1 H_3$	1.010 **(1.004)**	1.092 **(1.128)**	1.010 (**1.046**)	1.01
$C_2 H_5$	1.097 (**1.102**)	1.091(**1.084**)	1.090 **(1.112)**	1.10
Bond Angle [°]				
$H_6C_2N_1$	114.838 **(109.793)**	109.017 **(108.337)**	109.066 **(110.306)**	120
$C_2N_1H_5$	112.009 **(111.290)**	110.745 **(96.341)**	111.240 **(107.670)**	120
$H_3N_1H_4$	107.372 **(106.707)**	106.981(**104.556**)	107.343 **(106.556)**	120
Torsion Angle [°]				
$H_4N_1C_2H_7$	160.271(**178.821**)	169.685 **(177.622)**	175.069 **(177.627)**	---

Geometry parameters for the methyl amine as listed in Table 1 show that PW91 values obtained from all force fields are in good agreement with each other and with the literature values. The bond lengths are all within 0.01 Å of each other and, except for the literature values, the bond angles are all within 6 degrees. The larger discrepancy as observed when a comparison is made to the experimental data is probably due to the fact that these data are not specific for the CH_3NH_2 molecule studied here. Similarly, the torsion angles are within 15 degrees of each other. The similarity of the structures obtained from the different force fields (after PW91 geometry optimization) is confirmed when comparing their energies, which are , -827.475 , -827.867 and – 827.982 kcal/mol for CFF, DFF and UFF, respectively.

Table 1 also shows that there is an insignificant change between the PW91 input (shown in parentheses) and the PW91 optimized data. In this case, all of the force fields give structures that are in agreement with the PW91 and literature data. The similarity is also seen when comparing the initial and final minimum energies for the PW91 calculations, which varied by -10.908, -9.456 and -4. 982 kcal/mol for CFF, DFF and UFF, respectively.

3.2.   Benzocarboxylic acid (C$_6$H$_5$COOH)

A typical structure for the C$_6$H$_5$COOH molecule is shown in figure 4. The figure is also used in Table 2. The figure shows the atoms labels that are used in Table 2 and also as referred to in the discussion. Similarly, as was noted for the methylamine case, literature data only provides values that are for the general case for the Benzocarboxylic acid.
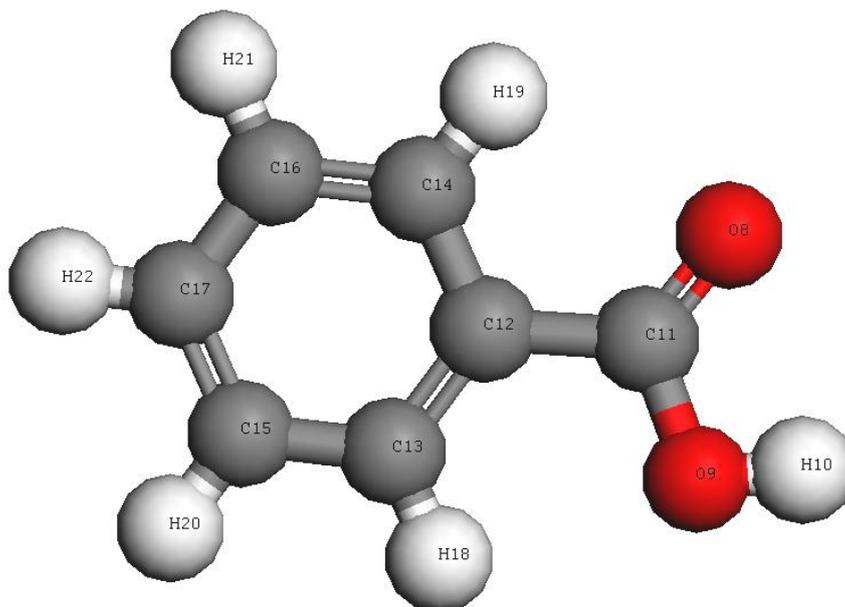

Figure 4: The C$_6$H$_5$COOH (Benzocarboxylic acid) molecule obtained by annealing using CFF and then geometry optimization with PW91.

Table 2: Selected bond lengths, bond angles and a torsion angle obtained from PW91 optimization when the initial geometry was obtained from the CFF, DFF and UFF. The initial values are shown in parentheses. In addition, literature values [35] are given in the final column.

Functional group	Force field			
Carboxylic Acid	Compass	Dreiding	Universal	Literature
Bond length [Å]				
$C_{11}=O_8$	1.224 **(1.500)**	1.222 **(1.510)**	1.222 **(1.221)**	1.22
$C_{11}-O_9$	1.367 **(1.509)**	1.367 **(1.509)**	1.367 **(1.368)**	1.43
$H_{10}-O_9$	0.975 **(1.111)**	0.975 **(1.110)**	0.975 **(1.014)**	0.96
Bond Angle [°]				
$C_{12}-C_{11}=O_8$	124.804 **(120.085)**	124.785 **(122.159)**	124.784 **(120.746)**	120
$C_{12}-C_{11}-O_9$	113.827 **(120.064)**	113.577 **(121.830)**	113.577 **(120.026)**	120
$O_8=C_{11}-O_9$	121.361 **(119.84)**	121.63 **(116.006)**	121.63 **(119.304)**	120
Torsion Angle [°]				
$C_{13}C_{12}C_{11=}O_8$	178.398 **(179.878)**	178.378 **(179.809)**	178.378 **(179.929)**	----

It is clear from Table 2 that the PW91 values obtained from all force fields are in semi quantitative agreement with each other and with the literature values. The bond lengths are all within 0.06 Å of each other and, except for the literature values, the bond angles are all within 8 degrees. The larger discrepancy with the experimental data is probably due to the fact that these data are not specific for the C_6H_5COOH molecule studied here. Similarly, the torsion angles are within 2 degrees of each other. The similarity of the structures obtained from the different force fields after PW91 geometry optimization is confirmed when comparing their energies, which are -2293.19, -2293.09 and -2293.10 kcal/mol for CFF, DFF and UFF, respectively.

Table 2 also shows that there is a small change between the PW91 input shown in parentheses and the PW91 optimized data. This shows that all of the force fields give structures that are in agreement with the PW91 and literature data. The difference in the initial and final minimum energies for the PW91 calculations differed by 1.87kcal/mol. The differences in the initial and final PW91 energies for DFF and UFF are larger 120.79 and 120.73 kcal/mol for DFF and UFF respectively indicating that these forcefields are not as accurate as CFF for this molecule. The difference in structural energies for CFF model is very small, which suggests that the input structure obtained from the forcefield annealed optimization is very close to PW91 structure.

In summary, all of the force fields provide a valid description of the C_6H_5COOH molecule.

3.3. CH_3NH_2-C_6H_5COOH

Since CFF yields results for C_6H_5COOH molecule that are in better agreement with PW91 than DFF and UFF ,only the results of the CFF are tabulated in Table 3. A comparison to DFF and UFF is made in the text.

Table 3: Selected intramolecular bond lengths, bond angles and torsion angles obtained from PW91 optimization of the $CH_3NH_2 – C_6H_5COOH$ complex when the initial geometry was obtained from the CFF. The initial values (i.e., the values obtained after annealing and geometry optimization with the CFF) are shown in parenthesis.

Amine		Carboxylic Acid	
Bond length [Å]			**[Å]**
N_1-C_2	1.609 (**1.458**)	C_{11}=O_8	1.234(**1.218**)
N_1-H_3	1.012 (**1.012**)	H_{10}-O_9	1.022 (**0.975**)
N_1-H_4	1.205(**1.008**)	C_{11}-O_9	1.344 (**1.360**)
C_2-H_6	1.109 (**1.102**)		
Bond Angles [°]			**[°]**
$H_3N_1H_4$	127.002 (**104.944**)	O_9-C_{11}=O_8	122.830 (**119.293**)
$H_3N_1C_2$	127.991 (**110.067**)	C_{11}-O_9-H_{10}	106.934 (**109.272**)
$H_7C_2H_5$	108.875 (**109.990**)	$C_{12}C_{11}$=O_8	121.976 (**127.874**)
$H_6C_2H_7$	105.766 (**107.512**)		
Torsion Angles [°]			
$H_3N_1C_2H_6$	177.259 (**176.628**)	$C_{14}C_{12}C_{11}$=O_8	179.164 (**177.595**)

Comparison between the data shown for the complex in Table 3 and that shown for the isolated molecules in Tables 1 and 2 show that changes in the amine bond lengths are below 0.2 Å. The bond angles however, have increased by up to 16°, except for the $H_6N_2H_7$ which changed by 1.5° after complexation. The torsion angles also show similar trend, except for PW91 prediction of the, which has increased by 17 °. On the other hand the results for the

C_6H_5COOH molecule where more agreeable than in the case of the amine. Here the bond lengths changes are not greater than 0.05°, the angles by less than 7° and the torsions by less than 3°.

Changes in the amine bond lengths due to complexation are also below 0.2 Å when using the DFF and UFF. There were also minimal changes in the bond angles, with an overall angle increase by 5 ° and 3° respectively, when compared to the initial geometry before complex interaction. Similar results were seen for the C_6H_5COOH. Here the bond lengths changed by less than 0.03 ° for DFF and 0.3 for UFF , while bond angles obtained from UFF also showed an increase of below 3.2°. However, DFF gave a rather large increase of 14 ° with respect to $C_{11}O_9H_{10}$ bond angle. The other two bond angles in this molecule changed by less than 3.6°. Changes in the torsion angles were lower than in CFF, by 3° for DFF and 0.83° for UFF.

Hence, all force fields yield internal geometries that are in reasonable comparison with the PW91 results and that yield similar trends when the molecules form the complex.

The largest difference between the $CH_3NH_2 - C_6H_5COOH$ structures obtained from the three different force fields is found in the intermolecular geometries. The structures obtained from the DFF and UFF methods are shown in figure 5 and 6 and can be compared with the structure obtained from the CFF structure in figure 2. It is seen that, in all cases, the nitrogen atom is located between the two oxygen atoms of the carboxylic group. One difference is that the nitrogen side of the amine ligand is facing the O-H side of the carboxylic acid group for DFF structure , while UFF agrees with CFF in that nitrogen is facing the =O side of the functional group or "inverted". However, the significant change is seen in the distances between the nitrogen atom and the carbonyl group. As seen from the data in Table 5, the CFF yields a CH_3NH_2 - C_6H_5COOH intermolecular separation that is far shorter than that predicted by both DFF and UFF.
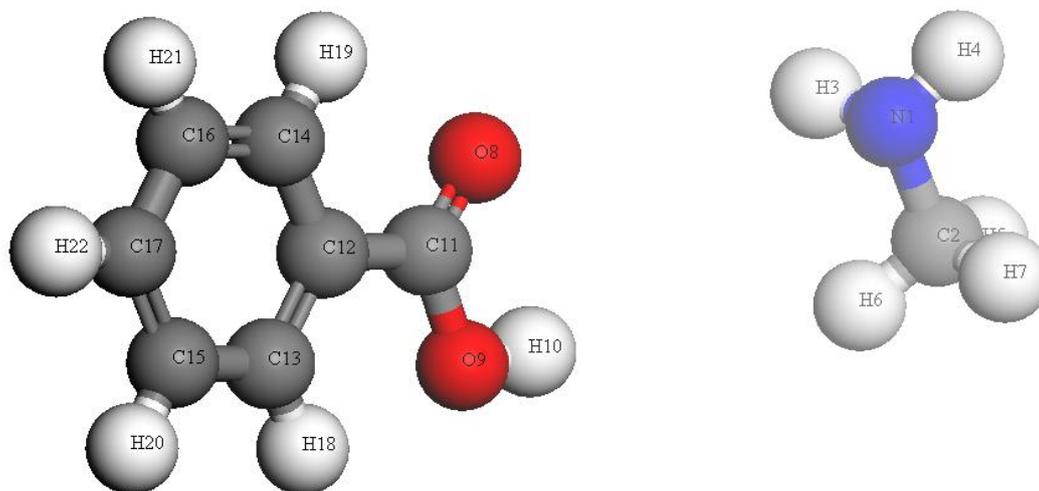
Figure 5: Structure used to model the carboxylic acid functionalized AC – amine complex. The structure was obtained by annealing using the DFF and then geometry optimization with PW91.
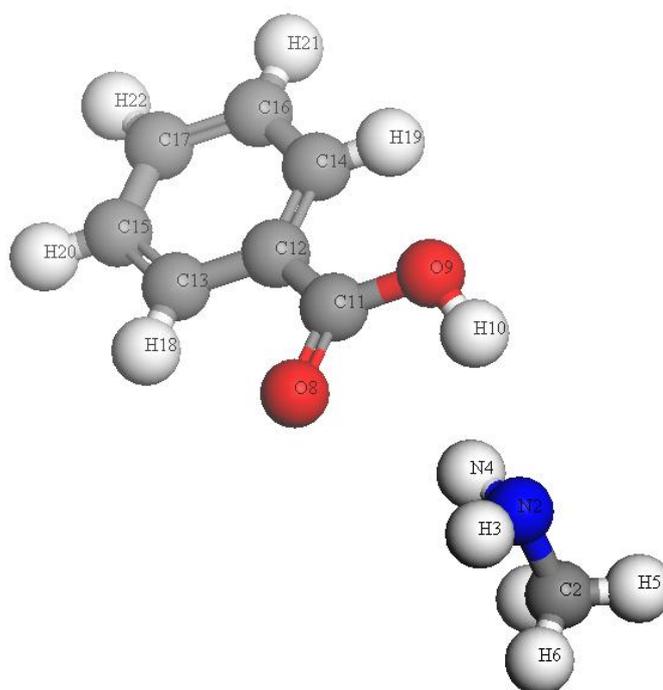

Figure 6: Structure used to model the carboxylic acid functionalized AC – amine complex. The structure was obtained by annealing using the UFF and then geometry optimization with PW91.

Table 4: Selected inter molecular bond lengths (distance in Å) obtained from PW91 optimization of the CH_3NH_2 – C_6H_5COOH complex when the initial geometry was obtained from the CFF, DFF and UFF. The initial values are shown in parenthesis.

	COMPASS	**DREIDING**	**UNIVERSAL**
$N_{1=}O_8$	3.108 (**3.164**)	6.472 (**3.159**)	5.756 (**4.185**)
$N_1.O_9$	3.187 (**3.401**)	7.108 (**3.655**)	5.989 (**3.162**)
N_1C_2	3.543 (**2.753**)	7.285 (**3.162**)	6.465 (**4.107**)
N_1H_{10}	2.224 (**1.779**)	6.158 (**2.258**)	5.172 (**5.439**)

3.4. Binding energies of methylamine to Activated carbon when functionalized with carboxylic acid, ester and ketone functional groups.

Table 5: Binding Energy values obtained by anealing with CFF ,UFF and DFF (in parenthesis) , and further optimization by PW91.

	COMPASS	**DREIDING**	**UNIVERSAL**
CARBOXYLIC	-13.167 (**-9.227**)	0 .0 (**-3.401**)	-0.715 (**-2.921**)
ESTER	-2.168 (**-3.102**)	-0.968 (**-10.192**)	-0.6 (**-22.767**)
KETONE	-1.245 (**-1.857**)	-2.767 (**-2.151**)	-0.6 (**-3.229**)

The PW91 binding energies for the CH_3NH_2 – C_6H_5COOH complex are -13.17, 0.0 and -0.72 kcal/mol when the initial optimization structures are obtained from CFF, DFF and UFF, respectively. This can be compared to the binding energies of -9.23, -3.40 and -2.92 kcal/mol obtained from the force fields. This shows that the CFF provides the best description for the complex geometry and binding energy.

The PW91 binding energies for the CH_3NH_2 – $C_6H_5COOCH_3$ and CH_3NH_2 – $C_6H_5COCH_3$ complexes are -2.168 and -1.25 kcal/mol when the initial optimization structures are obtained from CFF. This puts the carboxylic acid as the stronger binding group than an ester or ketone functional groups.

4. Conclusion

Structures and binding energies of methyl amine and ACs functionalized by functional groups (ketones, esters, and carboxylic acid) were studied using empirical forcefields and PW91 functional. In summary, all of the forcefields predicted valid structures for the methyl amine ligand and benzocarboxylic acid, ester and ketone. The best adsorption energies were given by CFF as it agreed well with PW91 energies and geometries. Results of the three empirical forcefields studied, the carboxylic acid showed the strongest binding energy than ketone and ester functional groups.

5. Acknowledgements

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