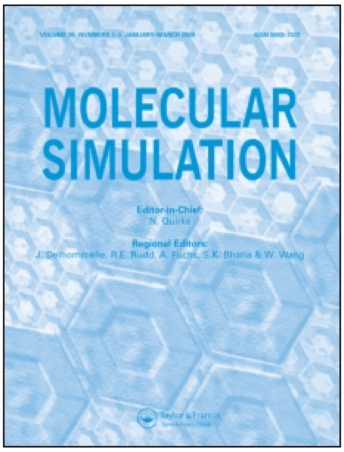

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The ground-state Na+ affinities of a series of substituted acetophenones: a DFT study

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The ground-state Na^+ affinities of a series of substituted acetophenones: a DFT study

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A detailed study of Na^+ affinities of a series of *para*-substituted acetophenones and their O—Na^+ counterparts was performed using density functional theory [Becke, Lee, Yang and Parr (B3LYP)] method using 6-311G(d,p) basis sets with complete geometry optimisation. The gas-phase O—Na^+ complex formation turns out to be an exothermic case and the local stereochemical disposition of Na^+ is found to be almost the same in each case. The presence of the *para*-substituent is seen to cause very little change in the Na^+ affinity relative to the unsubstituted acetophenones. Electron-releasing *p*-substituents increase it by 0.0105 hartree and electron-withdrawing *p*-substituents decrease it by 0.011 hartree. Computed Na^+ affinities are sought to be correlated with a number of computed system parameters such as the net charge on the Na^+ and the carbonyl oxygen of the Na^+ complexes and the net charge on the carbonyl oxygen of the free bases. The energetics, structural and electronic properties of the complexes indicate that the interaction between the Na^+ ion and a carbonyl base is predominantly an ion–dipole attraction and the ion-induced dipole interaction as well rather than a covalent interaction.

Keywords: B3LYP DFT; Gaussian; acetophenones; charge distribution; gas phase

1. Introduction

The interaction between a cation and a dipolar molecule is a particular type of acid–base interactions where the cation acts as an acid and the dipolar molecule as a base. The study of cation–dipole interactions has been found to be useful in a wide variety of fields [1–11]. Gas-phase studies of ion–molecule interactions provide information about the structure and bonding of complexes, which in turn are useful in the study of strong electrolytes and ionic solids [6]. Ion–molecule complexes are often the reaction products [7] of the scattering of high-energy neutral and ionic particles from surfaces. Cation–dipole interactions also find extensive applications [8, 9] in plasma chemistry, atmospheric chemistry, molecular biology, zeolite chemistry, in the field of molecular catalysis, mass spectrometry, etc. In view of their importance in various fields of chemistry, cation–dipole interactions have received considerable attention from both experimentalists [1–5,12–17] and theoreticians [18–22]. Still, sufficient experimental information is not available about the structure and interaction energies of cation–dipole complexes. The nature of bonding in these species, especially the role of valence interaction, has also not been carefully analysed. In recent years, studies of association of metal cations to understand organic compounds have attracted much attention for cation–π interactions [23]. Alkali metal ions were the first metal cations to be studied in the gas phase for their coordination properties. This can be understood by considering their relatively easy production under vacuum. In contrast with transition metal ions, their reactivity towards ligands is quite simple: in general, they form adducts, or clusters, which can be considered as ions 'solvated' by one or several ligands [24]. These ion–molecule complexes are involved in molecular recognition processes [25] and help in removing metal cations from contaminated media. These studies may be used to gain insight into many important biological processes [26–29], electron-transfer processes [30, 31] and more complicated biological systems. The purpose of the present work is twofold: (1) acetophenone and its substituted counterparts are one of the most deadly air pollutants and the present study may help in their removal and (2) to examine the relative sodium ion affinities (ΔE) of the *para*-substituted acetophenones containing both electron-withdrawing and electron-releasing substituents. The ground-state basicities of a series of substituted crotonaldehydes were reported in the literature [32]. The ground-state basicities of a series of substituted acetophenones were also studied [33]. Moreover, the ground-state Li^+ affinities of substituted crotonaldehyde [34] and substituted acetophenone [35] were studied. It was observed that the *ortho*- and *meta*-substituted acetophenones are less stable than the *para*-substituted counterparts. We have chosen the *para*-compounds as the case study to understand the nature and origin of variation in the relative magnitude of the Na^+ affinities (ΔE) to be expected in a series of aromatic carbonyls, namely acetophenones. We have calculated the gas-phase, ground-state Na^+ affinities (ΔE) of a number of *para*-substituted acetophenones by the B3LYP (DFT) method using 6-311G(d,p) basis sets

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Table 1. Computed total energies (hartree) of the free base (B) and the Na^+ complex (BNa^+), and sodium ion affinities [$\Delta E = (E_{\text{BNa}^+} - E_{\text{B}} - E_{\text{Na}^+})$, hartree] at the equilibrium geometry of the ground state.

	Total energy		
Molecule	B	BNa^+	ΔE
A, X = —H	− 384.9957	− 547.1436	− 0.0604
PMA, X = —CH_3	− 424.3241	− 586.4746	− 0.0630
PMyA, X = —OCH_3	− 499.5514	− 661.7046	− 0.0657
PAA, X = —NH_2	− 440.3725	− 602.5309	− 0.0709
PClA, X = —Cl	− 844.6173	− 1006.7619	− 0.0571
PCnA, X = —CN	− 477.2585	− 639.3968	− 0.0508
PNA, X = —NO_2	− 589.5494	− 751.6863	− 0.0494

Table 2. Computed net charge on the O-atom of the free base (B) and the Na^+ complex (BNa^+) and computed net charge on the sodium ion in the equilibrium ground state of the complex (BNa^+) and the free base (B).

	q_{O^-}		
Molecule	B	BNa^+	q_{Na^+}
A, X = —H	− 0.2963	− 0.4746	0.8648
PMA, X = —CH_3	− 0.2994	− 0.4809	0.8618
PMyA, X = —OCH_3	− 0.3064	− 0.4934	0.8565
PAA, X = —NH_2	− 0.3117	− 0.5046	0.8508
PClA, X = —Cl	− 0.2935	− 0.4758	0.8654
PCnA, X = —CN	− 0.2851	− 0.4654	0.8705
PNA, X = —NO_2	− 0.2821	− 0.4623	0.8721

Table 3. Computed hardness (hartree) of the free base (B) in the ground state.

Molecule	$\varepsilon_{\text{HOMO}}$	$\varepsilon_{\text{LUMO}}$	η
A	− 0.2565	− 0.0635	0.0965
PMA	− 0.2438	− 0.0505	0.0966
PMyA	− 0.2369	− 0.0522	0.0923
PAA	− 0.2197	− 0.0449	0.0873
PClA	− 0.2644	− 0.0733	0.0955
PCnA	− 0.2750	− 0.0968	0.0891
PNA	− 0.2775	− 0.1148	0.0813

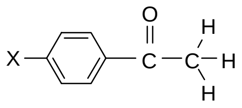
[36–38]. We have analysed the computed Na^+ affinity values to understand whether the pre-complex formation charge distribution local to the chromophore or post-complex relaxation of charge density or both are important in shaping the overall Na^+ affinity of the acetophenones. We have also looked into the possible origin of the small shift in the Na^+ affinities as one goes from the unsubstituted to the *para*-substituted acetophenones.

2. Computational details

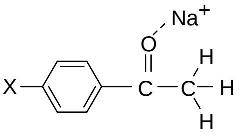
Calculations were performed using the Gaussian 03W software [36–38] and the B3LYP (DFT) method with 6-311G(d,p) basis sets. In all calculations, complete geometry optimisation has been carried out on the molecules both before and after Na^+ complex formation. Na^+ affinities were computed as ΔE for the reaction $\text{Na}^+ + \text{B} \rightarrow \text{BNa}^+$.

3. Results and discussion

The compounds studied are *para*-substituted acetophenones and their Na^+ complexes, which are given as follows:



[B]



[BNa^+]

X = –H, –CH_3, –OCH_3, –NH_2, –Cl, –CN, –NO_2

The molecules studied are listed in Table 1, along with their respective abbreviated names and total energies (hartree) of the free base (B) and the complex (BNa^+), and the computed Na^+ affinities (ΔE). Table 2 reports the computed net charge on the carbonyl oxygen atoms of the free base molecules and the Na^+ complexes both in their equilibrium ground state and the computed net charge carried out by Na^+ at the equilibrium ground state of the Na^+ complexes. From Table 2, it can be seen that the computed net charge on the Na^+ is in the range 0.8508–0.8721, showing that some migration of electron density to the added Na^+ has taken place. That this migration is not local and originates from all over the molecule is clearly reflected in the computed net charges on the carbonyl oxygen atoms of the Na^+ complexes as can be seen from Table 2. The oxygen atom still carries a net negative

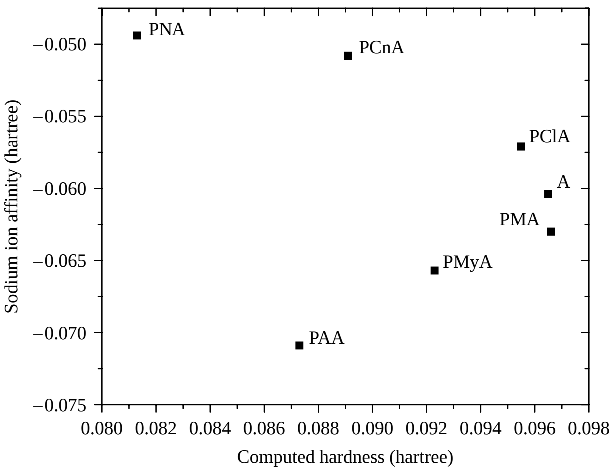
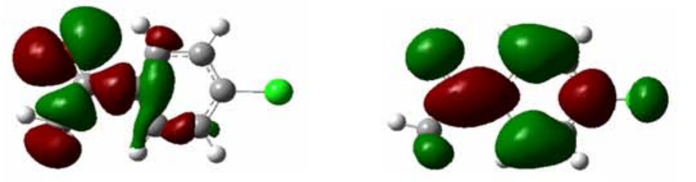
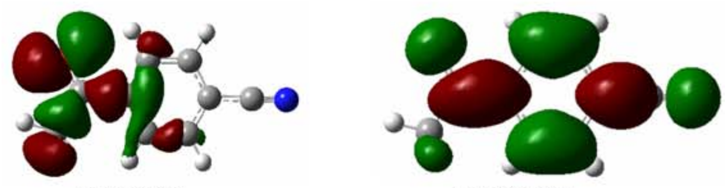


Figure 1. Plot of gas-phase sodium ion affinity vs. computed hardness.



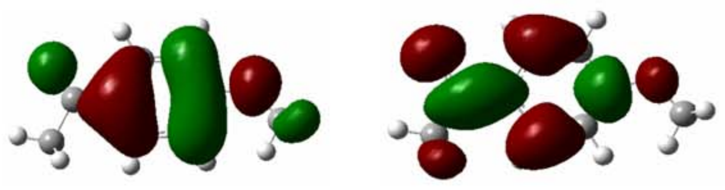
HOMO of PClA

LUMO of PClA



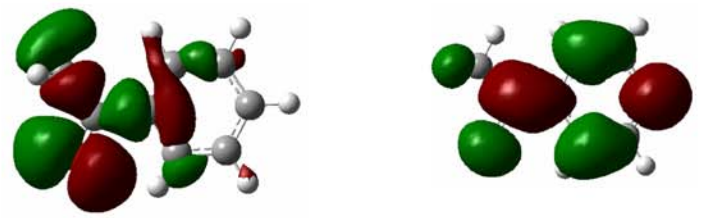
HOMO of PCnA

LUMO of PCnA



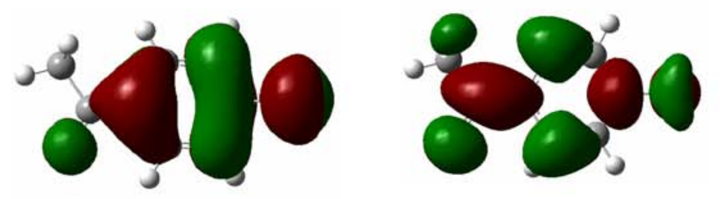
HOMO of PMyA

LUMO of PMyA



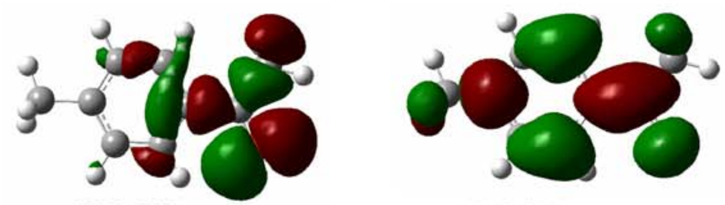
HOMO of A

LUMO of A



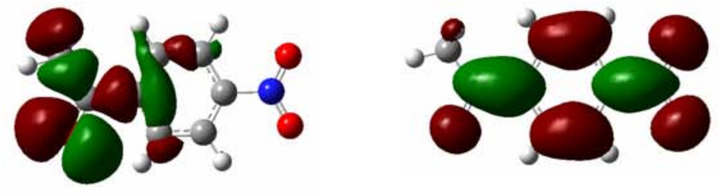
HOMO of PAA

LUMO of PAA



HOMO of PMA

LUMO of PMA



HOMO of PNA

LUMO of PNA

Figure 2. HOMO and LUMO structures of all the systems in the ground state.

Table 4. Geometrical features of the free base (B) and the complex (BNa^+).

	Free base	BNa^+			
Molecule	r(C—X)	r(C—X)	r(O—Na^+)	∠C—O—Na^+	∠C—C—O—Na^+
A	1.0843	1.0837	2.1082	168.9692	0.1276
PMA	1.5083	1.5038	2.1022	169.1096	− 0.1714
PMyA	1.3570	1.3366	2.0958	166.4708	1.5264
PAA	1.3833	1.3527	2.0849	167.7276	0.0170
PClA	1.7557	1.7363	2.1120	167.5617	0.0267
PCnA	1.4310	1.4298	2.1240	167.2879	− 0.0268
PNA	1.4833	1.4925	2.1257	167.3662	− 0.0159

Note: Length in Å and angle in degree.

charge, somewhat increased relative to the free base molecules. The magnitudes of charges of the complexes indicate that the interaction between Na^+ and the carbonyl base is predominantly an ion–dipole attraction and ion-induced dipole interaction as well rather than a covalent interaction. We have searched for the possibility of existence of correlation with a single global parameter of the entire molecule. As the global parameter, we have chosen the hardness $\eta = (I - A)/2 = (\varepsilon_{\rm LUMO} \sim \varepsilon_{\rm HOMO})/2$ listed in Table 3. From Table 3, it can be seen that no perfect correlation between the hardness and sodium ion affinity in the series could be made. In PNA, the η value is the lowest and its Na^+ affinity is the lowest, whereas, in PMA, its η value is the highest but its Na^+ affinity is not the highest. This is further revealed from Figure 1 where the gas-phase sodium ion affinity vs. computed hardness is plotted.

This also shows that both pre- and post-complex correlations with local charge densities in the immediate neighbourhood of the complex formation site are weak (Figure 2). It can therefore be anticipated that the Na^+ affinities of these carbonyl bases cannot be modelled or described by local properties of the carbonyl moiety only. Although it seems that there is a good but non-perfect linear correlation between the charge on oxygen in the free base (B) and the sodium affinities, still it must be shaped strongly by distant atom contribution in addition to the contribution from the carbonyl group.

The local characteristics at or around the carbonyl moiety are very nearly identical in each case. This is revealed from the data reported in Table 4 where some of the selected computed geometrical parameters are listed. The O—Na^+ bond length has a variation in the range 2.08–2.12 Å for all the substituted complexes. The C—O—Na^+ bond angle is in the range 166–169° in all the cases. Similarly, the torsion angle τ (C—C—O—Na^+) shows a variation of − 0.171–1.526° for all the substituted complexes. The carbonyl ring near invariant stereochemistry around the complex formation site of each base tends to suggest that the entire contributions from substituent effects to Na^+ affinity (ΔE) cannot be modelled properly unless contributions from far away centres are taken into account. The C—X bond length is slightly decreased (with the exception of PNA where it is slightly increased) in each case upon sodium ion complexation.

From Table 1, it can be seen that the ΔE values of all the substituted acetophenones are in the range − 0.049 to − 0.070 hartree. From the ΔE values, it is obvious that the gas-phase Na^+ complex formation turns out to be exothermic in each case. The electron-releasing substituents are seen to increase the computed ΔE's while electron-withdrawing groups have an opposite effect as expected. From Table 2, it is also clear that the charge density on the O-atom before complex formation is higher when X is an electron-releasing group. This favours complex formation. The reverse is the case with an electron-attracting group. This may be one of the reasons of the slight increase and decrease in ΔE values relative to unsubstituted acetophenones. Sodium ion is also optimised. The energy of sodium ion is − 162.0874 hartree.

It can be seen that the plot of the computed gas-phase sodium ion affinities against the computed net charge density on the carbonyl oxygen atom of the free bases

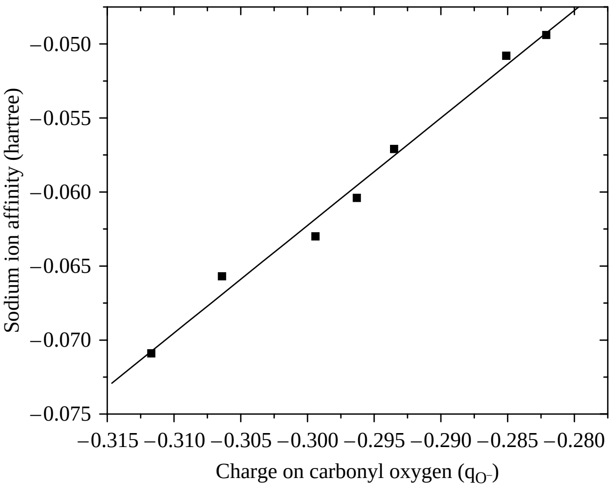


Figure 3. Plot of gas-phase, ground-state sodium ion affinity vs. charge on the carbonyl oxygen atom of the free bases.

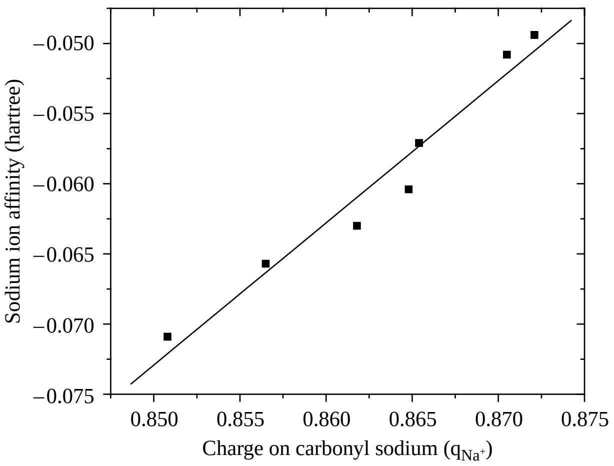


Figure 4. Plot of gas-phase sodium ion affinity vs. charge on sodium ion (q_{Na^+}) of the complex BNa^+.

(q_{O^-}) (Figure 3) and also the plot of sodium ion affinities vs. charge on sodium (q_{Na^+}) (Figure 4) of the fully relaxed BNa^+ are approximately linear. Thus, these reveal marginal linearity of the computed sodium ion affinities with respect to local parameters (i.e. q_{O^-} and q_{Na^+}). This indicates that both pre- and post-complex correlations with local charge densities in the immediate neighbourhood of the complex formation site are weak.

4. Conclusion

From the present theoretical study, it can be well concluded that the gas-phase sodium ion affinity of acetophenones and their *para*-substituted counterparts is spontaneous irrespective of their electron-releasing or electron-withdrawing nature. The electronic properties of the complexes indicate that the interaction is predominantly an ion–dipole attraction and ion-induced dipole interaction as well rather than a covalent interaction. The overall reactivity is fully explained by the distant atom contribution in addition to the contribution from the carbonyl group.

Acknowledgements

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