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The Li^+ Affinities of a Series of Substituted Crotonaldehyde in Their Lowest-Lying Excited Triplet State: A DFT Study

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ABSTRACT

DFT (B3LYP6-311G(d,p)) calculations of Li^+ affinities on a series of substituted crotonaldehyde (aliphatic unsaturated conjugated system) and their O–Li^+ counterparts were performed with complete geometry optimizations in the relevant excited state. The gas phase O–Li^+ complexation turns out to be the exothermic case and the local stereochemical disposition of the Li^+ is found to be almost the same in each case. The presence of substituent is seen to cause change of the Li^+ affinity (ΔE) relative to the unsubstituted crotonaldehyde. Electron releasing or electron withdrawing substituents change it by 12.55-37.65 Kcal/mol. Computed Li^+ affinities are sought to be correlated with a number of computed system parameters such as the net charge on the Li^+ and the carbonyl oxygen of the Li^+ complexes and the net charge on the carbonyl oxygen of the free bases and also the computed hardness of the free bases. The Li^+ ion induced shifts are in general red shifts except for the oxychloro compound where it is a blue shift. The energetics, structural and electronic properties of the complexes indicate that the interaction between the Li^+ 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; crotonaldehyde; charge distribution; Gas phase.

1. Introduction

Li^+ ion attachment mass spectrometry was being widely used in quantitative analysis of the atmospheric species [1-6]. The applicability of the method depends on the Li^+ ion affinity of the samples. Since then Li^+ ion affinities of perfluorocarbons and other compounds have been determined [7-15]. Recently the basicities of a series of substituted crotonaldehyde and acetophenone in their ground and excited triplet state and also the Li^+ affinities of substituted crotonaldehydes in their ground state and substituted acetophenones in their ground and excited triplet state were reported in the literature [16-22]. The Li^+ affinity introduces the idea that there must be some relation between the molecular electron density distribution and the affinity. This also implies that this property may vary from state to state of the same molecule due to some electronic transitions which are accompanied by extensive reorganization of molecular electronic charge distribution. The purpose of the present study is (1) to calculate the same for a series of aliphatic unsaturated conjugated systems, viz, substituted crotonaldehydes which are carcinogenic, mutagenic, air, water and food pollutants and their properties in the lowest excited triplet state is not available in the literature and this study may help the experimentalist, (2) to examine the relative lithium ion affinities (ΔE) of the substituted crotonaldehyde containing both electron withdrawing and electron releasing groups in the relevant excited state.. In an effort to understand the nature and origin of variation in the relative magnitude of the Li^+ affinities (ΔE) to be expected in a series of aliphatic unsaturated conjugated carbonyls, namely, crotonaldehyde, we have calculated the gas phase Li^+ affinities (ΔE) in the lowest excited triplet state of a number of substituted crotonaldehydes by B3LYP (DFT) method using 6–311G(d,p) basis sets [23]. We have analyzed the computed Li^+ affinity values, transition energies 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 Li^+ affinity of the crotonaldehydes in a particular state. We have also analyzed the kind and extent of spectral shift caused by complex formation in the relevant state. In a particular state the possibility of correlating the Li^+ affinity with the global hardness of the molecules is also explored. We have also looked into the possible origin of the small shift in the Li^+ affinities as one goes from the unsubstituted to the substituted crotonaldehydes in the lowest excited triplet state.

2. Computational details

Calculations were performed using Gaussian 03W software [23] and B3LYP (DFT) method with 6–311G(d,p) basis sets. In all calculations complete geometry optimization has been carried out on the molecules both before and after Li^+ complex formation in the relevant state. Li^+ affinities were computed as ΔE for the reaction $Li^+ + B \rightarrow BLi^+$.

3. Result and discussion

The molecules studied are listed in Table 1 along with their respective abbreviated names and total energies (hartree) of free base (B) and the complex (BLi^+) and computed Li^+ affinities (ΔE) of the lowest excited triplet state. Table 2 reports the computed net Mulliken charge on the carbonyl oxygen atoms of the free base molecules and the Li^+ complexes both in their equilibrium lowest excited triplet state as well as the computed net Mulliken charge carried out by Li^+ at the equilibrium excited triplet state of the Li^+ complexes. Atomic charge is not an observable quantum mechanical property. All methods for computing the atomic charges are necessarily arbitrary. Electron density among the atoms in a molecular system is being partitioned. Mulliken population analysis computes charges by dividing orbital overlap equally between the two atoms involved. Therefore the values are non-unique. Still, it is widely used. NBO calculations on some members of the present series are performed but no significant changes are found from Mulliken density. So the results are analysed on Mulliken density basis. From Table 2, it is seen that the computed net charge on the Li$^+$ is medium in each case and is in the range 0.69 – 0.78 showing that some migration of electron density to the added Li$^+$ 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 Li$^+$ complexes as seen from Table 2. The oxygen atom still carries a net negative charge, somewhat increased relative to the free base molecules. The magnitudes of charges of the complexes indicate that the interaction between Li$^+$ and the carbonyl base in the lowest excited triplet state is predominantly an ion–dipole attraction and ion-induced dipole interaction as well rather than a covalent 120 interaction. 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. It can therefore be anticipated that the Li$^+$ affinities of these carbonyl bases can not be modelled or described by local properties of the carbonyl moiety only. The charge on oxygen in OxCR is highest and its lithium affinity is lowest, the same in NCR is lowest and its lithium affinity is higher in the series but lower than the unsubstituted crotonaldehyde. No correlation is followed by the substituents. Therefore the lithium affinity of the series 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 3 where some of the selected computed geometrical parameters are listed. The O–Li$^+$ bond length has a variation in the range 1.67 – 1.75 Å for all the substituted complexes. The C-O-Li$^+$ bond angle is in the range 162 – 187^0 in all the cases. Similarly the torsion angle τ (C-C-O-Li$^+$) shows a small variation (141 –177^0). The carbonyl ring near invariant stereochemistry round the complex formation site of each base tends to suggest that the entire contribution from substituent effects to Li$^+$ affinity (ΔE) can not be modelled properly unless contribution from far away centres are taken into account. The C-X bond length is little decreased (with the exception of CR and OxCR where it is slightly increased) in each case upon lithium ion complexation.

From Table 1 it is seen that the ΔE values of all the substituted crotonaldehydes are in the range -0.03 to -0.11 hartree. The ΔE for the unsubstituted base is -0.094 hartree indicating that the gas phase Li$^+$ 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 O-atom before complex formation can not be correlated with the Li$^+$ ion affinity in the case of unsubstituted and substituted crotonaldehydes. Table 4 shows the computed transition energies [$^1S_0 \rightarrow T_1$ (lowest excited triplet state)] and shifts caused by Li$^+$ complex formation. It is clear from the data that in all cases the Li^+ induced shifts (LIS) are red shifts except for the oxychloro compound where it is a blue shift. These data refer to the gas phase Li^+ complex formation of the isolated base molecules without any additional effects caused by solvation. We have searched for the possibility of existence of correlation with a single global parameter of the entire molecule in the relevant state. As the global parameter we have chosen the hardness, $\eta = (I - A)/2 = (\varepsilon_{LUMO} \sim \varepsilon_{HOMO})/2$ listed in Table 5 along with the respective ground state values. From Table 5 it is seen that in the triplet state the η value is highest for AMCR and its Li^+ affinity is also highest but this correlation is not followed by other members of the series. This is further revealed from the fig.1 where Li^+ affinity is plotted against the computed hardness. Here linearity is not followed .We have searched for the HOMO and LUMO structures(shown in the fig.2) and have seen that Li^+ ion might be attracted by both aldehyde oxygen and substituents in the series.The LUMO of these systems support this.

4. Conclusion

From the present theoretical study it can be well concluded that the gas phase lithium ion affinity of crotonaldehydes and its substituted counterparts in the lowest excited triplet state is spontaneous irrespective of their electron releasing or 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 distant atom contribution in addition to the contribution from the carbonyl group.

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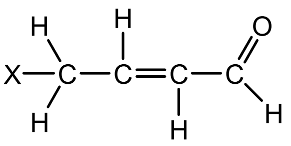
Table 1

Computed total energies (hartree) of free base (B) and Li$^+$ complex (BLi$^+$) and lithium ion affinities [$\Delta E = (E_{BLi^+} - E_B - E_{Li^+})$, hartree] at the equilibrium geometry of the lowest excited triplet state(E_{Li^+} = - 7.284905 hartree) by B3LYP 6-311G(d,p) method.1 hartree = 627.5095 Kcal/mol.

Molecule	Total energy		ΔE
	B	BLi$^+$	
CR,x= -H	-231.1950	-238.5739	-0.0940
ECR,x= -C_2H_5	-309.8404	-317.2244	-0.0990
ACR,x= -NH_2	-286.5552	-293.9408	-0.1007
AMCR,x= -NH (CH_3)	-325.8710	-333.2664	-0.1105
NCR,x= -NO_2	-435.7491	-443.1136	-0.0796
CxCR,x= -CN	-323.4536	-330.8389	-0.0866
OxCR,x= -OCL	-766.0409	-773.3597	-0.0339



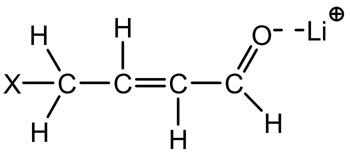


Table 2

Computed net charge on O-atom (q_o^-)of free base (B) and Li^+ complex (BLi^+) and computed net charge on (q_{Li^+}) lithium at the equilibrium geometry of the lowest excited triplet state of the complex (BLi^+) and free base (B).

Molecule	q_o^-		q_{Li^+}
	B	BLi^+	
CR	-0.2005	-0.4159	0.7848
ECR	-0.1434	-0.4190	0.7313
ACR	-0.1402	-0.4628	0.7317
AMCR	-0.1404	-0.4890	0.6987
NCR	-0.1204	-0.4273	0.7832
CxCR	-0.1256	-0.4063	0.7860
OxCR	-0.2763	-0.4174	0.7856

Table 3

Geometrical features of the free base (B) and the complex (BLi^+) (Length in Å and angle in ^{0}) at the equilibrium geometry of the lowest excited triplet state.

Molecule	Free base(B)	Complex(BLi^+)			
	r(C – X)	r(C – X)	r(O – Li^+)	<C – O – Li^+	<C-C-O-Li^+
CR	1.0872	1.0928	1.7391	187.10	166.90
ECR	1.5381	1.5374	1.7356	173.90	172.51
ACR	1.4724	1.4688	1.6923	177.08	176.46
AMCR	1.4665	1.4598	1.6714	179.94	177.48
NCR	1.5477	1.5009	1.7390	170.05	141.52
CxCR	1.4680	1.4639	1.7522	162.07	141.87
OxCR	1.3710	1.4433	1.7420	167.68	-166.89

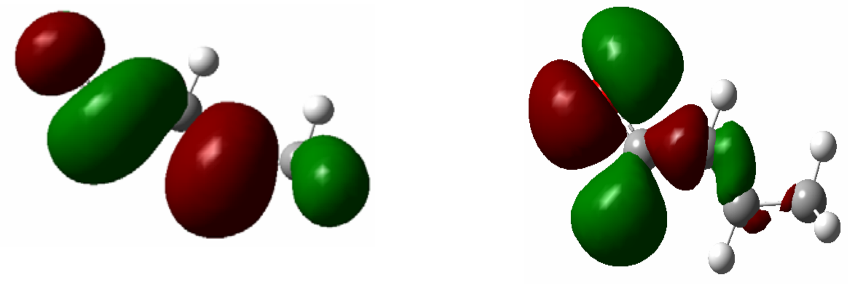
Table 4. Computed adiabatic transition energies ($^1S_o \rightarrow T_1$) (hartree) and Li$^+$ ion-induced shifts (LIS, hartree) in the lowest excited triplet state.

Molecule (^1S_o) → (T_1)	Transition energy		LIS
	B	BH$^+$	
CR	0.1054	0.0977	-0.0076
ECR	0.1062	0.0951	-0.0110
ACR	0.1042	0.0905	-0.0136
AMCR	0.1043	0.0811	-0.0231
NCR	0.0989	0.0938	-0.0050
CxCR	0.1010	0.0888	-0.0122
OxCR	0.0437	0.0924	+0.0487

Table 5. Computed hardness (hartree) of the free base (B) in the lowest excited triplet state. The values in the parenthesis are for the respective ground state.

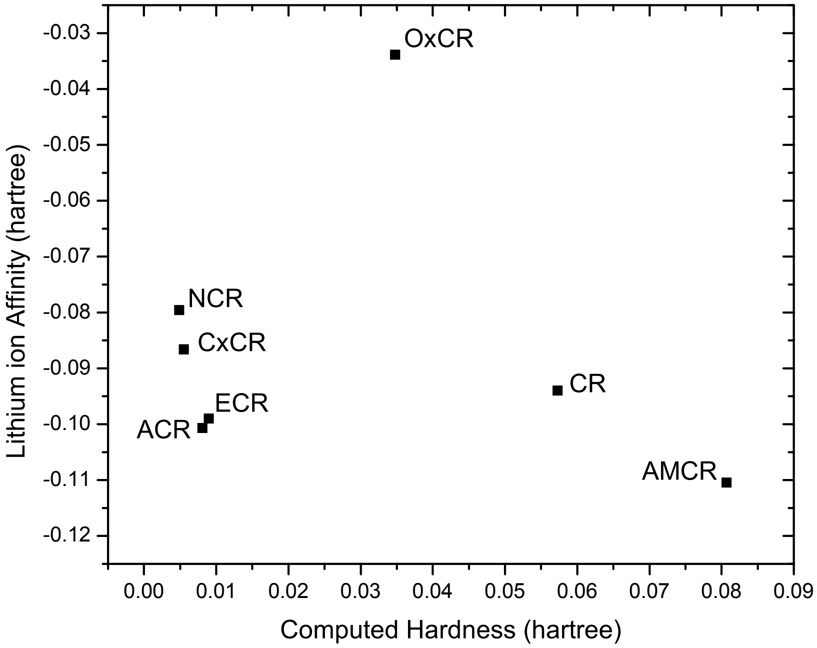
Molecule	ε_{HOMO}	ε_{LUMO}	η
CR	-0.2947 (-0.2488)	-0.1801 (-0.0547)	0.0573 (0.0970)
ECR	-0.1622 (-0.2476)	-0.1802 (-0.0549)	0.0090 (0.0963)
ACR	-0.1663 (-0.2495)	-0.1827 (-0.0577)	0.0081 (0.0959)
AMCR	-0.1661 (-0.2357)	-0.1822 (-0.0529)	0.0807 (0.0913)
NCR	-0.1941 (-0.2697)	-0.2039 (-0.1356)	0.0049 (0.0670)
CxCR	-0.1887 (-0.2682)	-0.1998 (-0.0791)	0.0055 (0.0945)
OxCR	-0.2785 (-0.2651)	-0.2088 (-0.0996)	0.0348 (0.0827)

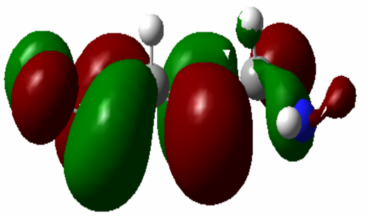
Figure 1 Plot of computed hardness versus Lithium ion affinity.



HOMO of CR

LUMO of CR





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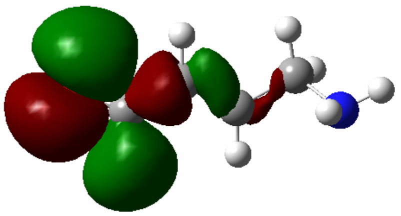
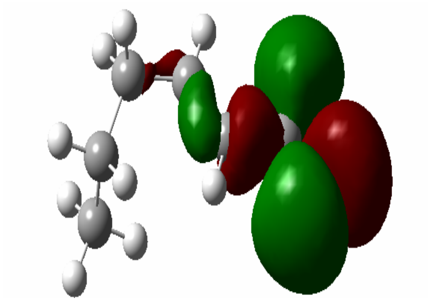


LUMO of ACR



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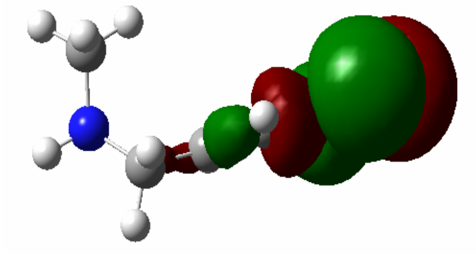

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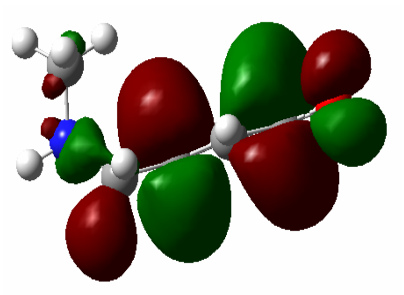

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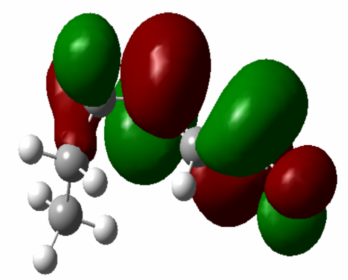
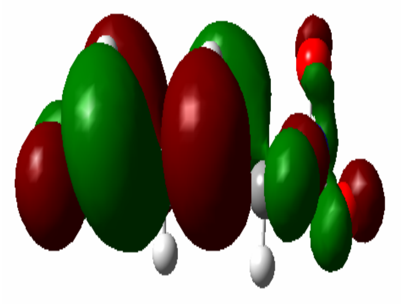
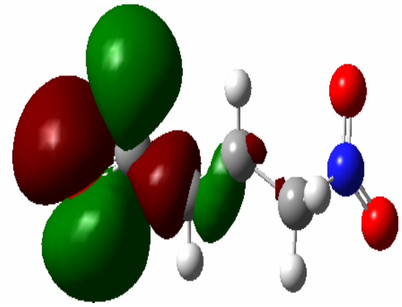


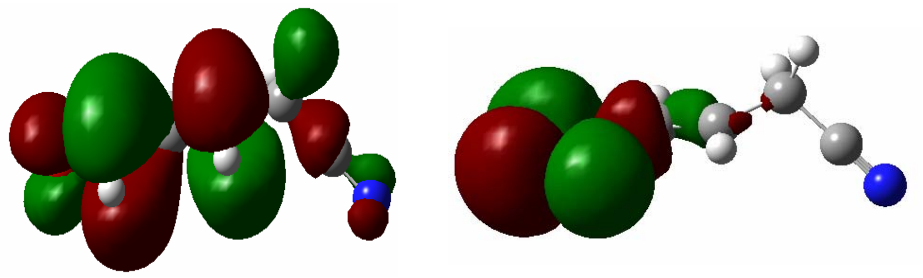
LUMO of AMCR



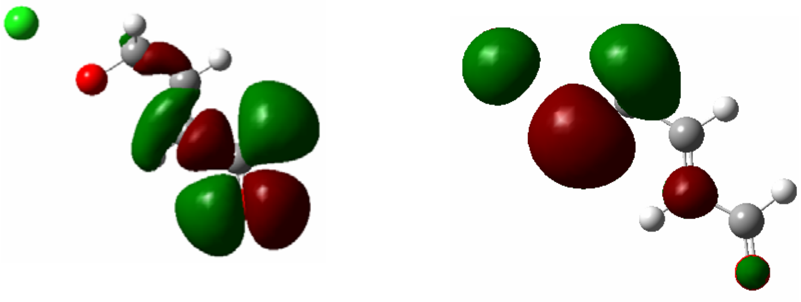
HOMO of NCR



LUMO of NCR



HOMO of CxCR LUMO of CxCR



HOMO of OxCR LUMO of OxCR

Figure 2 HOMO and LUMO of all the systems in the lowest excited triplet state.