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Estimating the Binding Ability of Onium Ions with CO_2 and π Systems: A Computational Investigation

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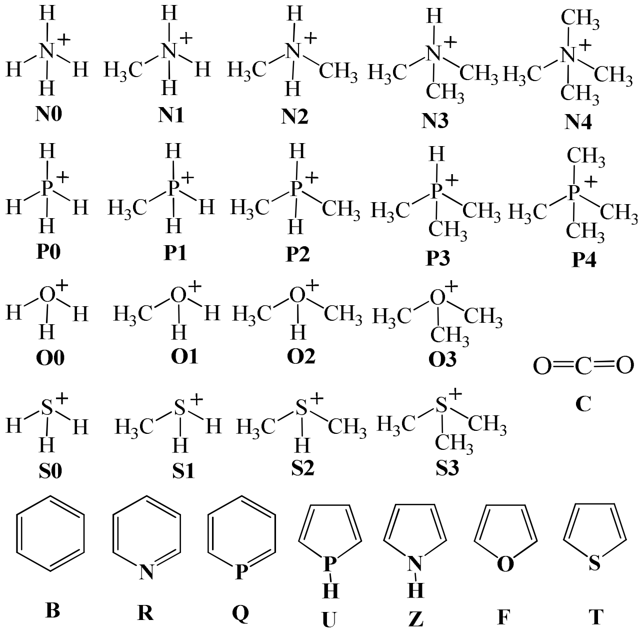
Density functional theory (DFT) calculations have been employed on 165 complexes of onium ions (NH_4^+, PH_4^+, OH_3^+,SH_3^+) and methylated onium ions with CO_2, aromatic (C_6H_6) and heteroaromatic (C_5H_5X, X = N, P; C_4H_5Y, Y = N, P; C_4H_4Z, Z = O, S) systems. The stability of CO_2···onium, CO_2···π and onium···π complexes was shown to be mediated through various noncovalent interactions such as hydrogen bonding, NH-π, PH-π, OH-π, SH-π, CH-π and π-π. We have discussed 17 complexes wherein the proton transfer occurs between onium ion and heteroaromatic system. The binding energy is found to decrease with increasing methyl substitution of the complexes containing onium ions. Binding energy components of all the noncovalent complexes were explored using localized molecular orbital energy decomposition analysis (LMO-EDA). The CO_2···π complexes were primarily stabilized by the dispersion term followed by contributions from electrostatic and polarization components. In general, for onium ion complexes with CO_2 or π systems, the electrostatic and polarization terms primarily contribute to stabilize the complex. As the number of methyl groups increases on the onium ion, the dispersion term is seen to have a key role in stabilization of the complex. Quantum Theory of Atoms In Molecules (QTAIM) analysis and charges based on Natural Population Analysis (NPA) in various complexes have also been reported in order to determine the nature of noncovalent interactions in different complexes.

1. Introduction

Extensive experimental and theoretical studies have elucidated the importance of noncovalent interactions involving onium ions and aromatic systems in material chemistry, structural biology and also in biological processes.[1-7] Principally, noncovalent interactions such as cation-π, π-stacking and anion-π interactions involving aromatic rings play a fundamental role in many areas of modern chemistry including the design of novel functional materials.[7-14] Aromatic systems have been established as sensitive gas capture[15-21] and gas sensor materials[21,22] operating via noncovalent interactions. Several aromatic systems form integral part of linker molecules in novel metal-organic framework (MOFs) materials with enhanced affinity for CO_2 adsorption.[23-25] For instance, Rosi and coworkers [26] have studied the CO_2 uptake capacity of MOF's through cation exchange method, in the presence of methylated onium ions operating via various noncovalent interactions. Interestingly Cundari et al.[27-31] concluded that acid/base interactions are the principal chemical force by which CO_2 binds to proteins.



Scheme 1 Onium ions, CO_2 and π systems considered in this study.

Zhang and coworkers[32] reported high CO_2 affinity and selectivity with exposed nitrogen of the charged framework in ionic porous coordination framework. Several studies have been reported that aromatic and heteroaromatic π systems bind with

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† Electronic Supplementary Information (ESI) available: Tables and figures of QTAIM analysis, NPA charge transfer and binding energies at M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) level of theory. LMO-EDA analysis at M06-2X/6-31G(d) level of theory. See DOI: 10.1039/b000000x/.

CO_2 through physisorption.[16,17,33-38] Froudakis and coworkers studied interactions between CO_2 and N-containing organic heterocycles.[39] The interactions were shown to occur at two different sites and via different mechanisms, one through Lewis acid-Lewis base interactions and the other, via hydrogen bonding. Torrissi et al.[16,17] have reported a number of weak noncovalent interactions between the CO_2 molecule and a range of functionalized aromatic molecules involving -NO_2, -NH_2, -OH, -SO_3H, -COOH, halogen and methyl substituents. Sun and coworkers[40] have studied π-π interactions between CO_2 and benzene, pyridine and pyrrole revealing that electron correlation plays a critical role in describing the interactions of CO_2 with aromatic molecules. In this context understanding the interaction of CO_2 with different nonmethylated as well as methylated onium ions and substituted aromatic systems becomes important.

Traditionally interactions involving onium ions have taken into account to understand the binding between different aromatic and positively charged amino acids in proteins.[41-43] Moetner and coworkers[44] evaluated the binding energies of NH_4^+ and $MeNH_3^+$ with ethylene and benzene derivatives showing that these interactions are stronger than typical hydrogen bonds. Kim and coworkers[45] have extensively studied the noncovalent interactions between aromatic ring and quaternary ammonium compound. their studies depict NH-π and CH-π interaction with the benzene,[46] high selectivity of ammonium ion over K^+ for binding to pyrazole receptor[47] besides delineating the interaction between substituted ammonium cation and aromatic system.[48] Olivier et al. showed that ammonium-π interactions are also useful in selective adsorption of carbon nano tubes (CNTs) on to polymer brushes.[49] A recent study by Rapp et al.[50] reveals that cation–π interactions of methylated ammonium ions are modulated by a change in the methylation state and interaction geometry.

While a substantial number of studies on ammonium ion interaction with aromatic systems have been reported,[1,51,52] studies on interactions between other onium ions and π systems are rather limited.[53-57]A few studies involving phosphonium, hydronium and sulfonium ions are briefly described below. It is explored that the potential use of multiple triphenyl phosphonium (TPP)[58] moieties for the internalization of a pro-apoptotic tri peptide (KLA) into intact cancer cells is governed by triphenylphosphonium cations.[59] Triphenylphosphonium cations with long alkyl chains, are found to accumulate in mitochondria of rats.[60] These cations are able to conjugate to thiophenefluorophore or to a cyclometalated Pt (II) complex[61,62] which is generally observed in the nucleoli of cells and cytoplasm. A CH-π interaction is observed in the crystal structure of BPh_4^-, benzyl triphenylphosphonium salts and also in choline tetra phenyl borate, Me_3N^+-CH_2-$CH_2OHBPh_4^-$.[63] Interaction of oxygen containing onium ions with π systems were studied by several groups.[64-66] The π-interactions of OH bonds with aromatic acceptors are recognized in H_2O solvates[67] and in benzene/water gas-phase clusters.[68] Hydrated protons and hydronium ions (OH_3^+) are crucial players in many chemical and biological processes. OH_3^+ is an active protonating species in an acid-catalyzed reaction. Arene rings could participate in the biological transport of protons via π-complexed hydronium ions.[64] Neutron crystallographic analysis at near-atomic resolution of both reduced and oxidized forms of perdeuterated *Pyrococcusfuriosus* rubredoxin protein study shows that the favorable hydrogen bonding energetics of a hydronium ion plays an important role in both the stability of rubredoxin and its redox properties.[69] An exhaustive X-ray/neutron crystallography analysis by Kovalevsky et al.[70] showed broad implications of hydronium ions in biological systems. The sulfonium ion-π interactions play a primary role in determining substrate specificity. An examination of the crystal structure of S-Adenosylmethionine decarboxylase (AdoMetDC) with 5ˈ-deoxy-5ˈ-(dimethylsulfonio) adenosine (MMTA) shows that the sulfonium center is at a favorable distance and geometry to form a cation-π interaction with Phe223.[53,71] In thiourea-catalysed ring opening of episulfonium ions with indole derivatives, the cationic transition state is stabilized through the cation-π interaction between the extended aromatic residue on the catalyst and the acidic α-protons in the episulfonium ion.[72] The stereo chemistry of glycosylsulfonium ion makes a significant contribution in mechanistic studies on glycosylation reactions.[73]

Thus a large number of studies have been reported on onium ion···π interactions, using quantum mechanical,[74-80] molecular dynamics,[81] Monte Carlo simulation method,[82] Car-Parrinello molecular dynamics method[83] and QMMM.[84] Although these studies primarily focused their attention on determining the optimal geometries and interaction energies for different model systems, a comprehensive understanding of the physical mechanism of cation-π interactions involving onium ions still remains elusive. The current study aims at understanding the physical mechanism of binding of ammonium, phosphonium, hydronium and sulfonium ions in both methylated/non methylated forms with CO_2 and seven different aromatic and heteroaromatic systems including benzene, pyridine, phosphinine, phosphole, pyrrole, furan and thiophene. As discussed earlier, considering its potential applications, the interactions between CO_2 and π systems is also explored. Scheme 1 provides a pictorial representation of all the different systems considered in our study. The preferential binding modes of different complexes along with an analysis of the various factors contributing to their binding energies are delineated using energy decomposition analysis. The impact of increasing methylation and the consequent size effects are systematically explored in different onium ions.

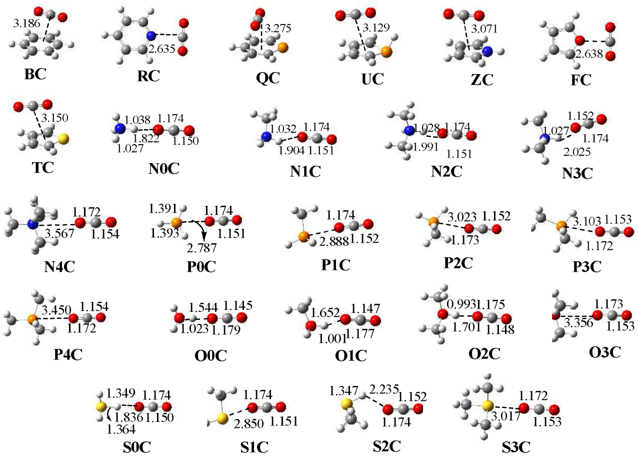

Fig. 1 Geometrical parameters (distances in Å) of CO_2 complexes computed at M06-2X/6-31G(d) level of theory.

2. Methodology

All possible orientations of ammonium, phosphonium, hydronium and sulfonium ions as well as their incrementally methylated forms interacting with CO_2 (C), benzene (B) and six other heteroaromatic systems pyridine (R), phosphinine (Q), phosphole (U), pyrrole (Z), furan (F), and thiophene (T) in different conformations were optimized at M06-2X/6-31G(d) level of theory.[85] In order to understand the CO_2 binding affinity with aromatic system we have optimized their complexes in all possible conformations at M06-2X/6-31G(d) level of theory. M06-2X appear to be an acceptable functional due to its satisfactory treatment of dispersion interactions.[86,87] Mackie and DiLabio have shown that M06-2X functional with 6-31G(d) basis set provides reasonable results for systems including those which are dominated by dispersion, hydrogen bonding and a mixture of both interactions.[87] Frequency calculations were done to ascertain the nature of stationary points on the potential energy surface (PES). Further single point calculations have been carried out on the optimized geometries at M06-2X/6-311++G(d,p) level of theory to provide more reliable energies for all the complexes studied. The most stable structures and their energies were reported in Figures 1-7 and Tables 1-5. The optimized geometries of onium ion complexes with aromatic systems were classified into two types: cation-π complexes and proton transfer complexes. In the cation-π complexes, the onium ion was located above the plane of the aromatic ring, with hydrogen atoms directed toward the ring. In proton transfer complexes, the proton is transferred from onium ion either to the heteroatom of the ring or to the carbon of the ring. The binding energy (BE) of each complex is calculated as the difference between the sum of total energies of the monomer A and monomer B and the total energies of the complex AB in the geometry of the complex as given in equation 1.

$$\mathrm{BE} = (\mathrm{E_A} + \mathrm{E_B}) - \mathrm{E_{AB}} \qquad (1)$$

Where E_A is the total energy of the monomer A, E_B is the total energy of the monomer B and E_{AB} is the total energy of the complex AB. The binding energy so obtained was further corrected for basis set superposition error (BSSE) by counterpoise method of Boys–Bernardi.[88] We have employed NPA[89,90] to examine the charge transfer in the complexes studied. NPA has been developed to calculate atomic charges and orbital populations of molecular wave functions in general atomic orbital basis sets. It is an alternative to the conventional Mulliken population analysis, and seems to exhibit improved numerical stability and to better describe the electron distribution in compounds of high ionic character. All the calculations were done using the Gaussian 09 package.[91]

The topological properties of the electron density can be mapped with the help of the QTAIM theory developed by Bader and coworkers.[92,93] QTAIM analysis was performed to investigate and characterize the nature of noncovalent interactions of different complexes at M06-2X/6-311++G(d,p) level of theory on the previously mentioned optimized geometries using AIM 2000 program.[94,95] The electron density at critical points (CP, (3,–1)) is taken into account for the characterization of chemical bonding.[96] The individual contribution of various factors to the binding energy of all the complexes has been investigated by employing localized molecular orbital energy decomposition analysis (LMO-EDA).[97] In case of LMO-EDA, the interaction energy (INT) of any complex at a given instant is analyzed for contributions from electrostatic (ES), exchange (EX), repulsion (REP), polarization (POL) and dispersion (DIS) energies. The M06-2X/6-31G(d) optimized geometries were further used to perform LMO-EDA at same level using the option "run type = EDA" available in the GAMESS software.[98] The total interaction energy is calculated as the sum of the electrostatic, exchange, repulsion, polarization and dispersion components as shown in the equation 2.

$$\mathrm{E_{INT}} = \mathrm{E_{ES}} + \mathrm{E_{EX}} + \mathrm{E_{REP}} + \mathrm{E_{POL}} + \mathrm{E_{DIS}} \qquad (2)$$

By definition the gas phase basicity is the negative of the free energy change while the proton affinity is the negative of the corresponding enthalpy change.[99] Proton affinity (PA) values of all the parent molecules in the current study have been evaluated at a temperature of 298.15 K. Higher the proton affinity, the stronger the base and the weaker the conjugate acid in the gas phase[100] which in turn explains the ability of proton transfer between onium ion and aromatic system. Moreover, the methyl cation affinity (MCA) is also used as a measure of the negative of the reaction enthalpy.[101] Methyl cation affinity values are much better descriptors of catalytic activity than either proton affinity or pKa values.[102,103] In order to gauge the propensity of proton transfer of a system, the proton affinity and methyl cation affinity data is computed at M06-2X/6-31G(d) level of theory. The proton affinities and methyl cation affinities are calculated for all parent molecules as the reaction enthalpies of the transformations shown in the equations 3 and 4 given below.

$$\mathrm{H^+} + \mathrm{B} \overset{\mathrm{PA}}{\rightleftharpoons} \mathrm{BH^+} \qquad (3)$$

$$\mathrm{CH_3^+} + \mathrm{B} \overset{\mathrm{MCA}}{\leftrightharpoons} \mathrm{BCH_3^+} \qquad (4)$$

B is the parent molecule. The proton affinities and methyl cation affinities are computed using the equation 5.

$$\mathrm{PA\ or\ MCA} = -\Delta\mathrm{H} = \Delta\mathrm{E_{ele}} + \Delta\mathrm{ZPE_{ele}} + \frac{5}{2}\,\mathrm{RT} \qquad (5)$$

Where $\Delta\mathrm{E_{ele}} = [\mathrm{E(B)} - \mathrm{E(BH^+)}]$, $\Delta\mathrm{ZPE_{ele}} = [\mathrm{ZPE(B)} - \mathrm{ZPE(BH^+)}]$ refers to the zero-point energy, and the constant 5RT/2 is the classical estimation of the effect of gaining three transitional degrees of freedom (3RT/2) for the proton plus RT, the PV term for the proton.

3. Results

In the first part of the results section the optimized geometries and binding energies of all the complexes taken as part of the study are analyzed.

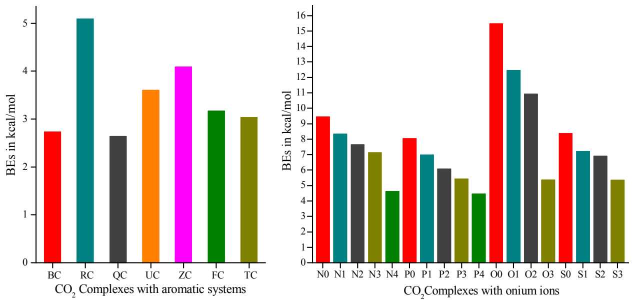

Fig. 2 BSSE corrected binding energies of CO_2 complexes computed at M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) level of theory.

Following this the results of NPA, QTAIM analysis along with the comparison of the different components of binding energy evaluated using LMO-EDA analysis are emphasized in the discussion section. The role of proton affinities and methyl cation affinities of the parent molecules in the formation of the complexes where proton transfer is seen is also described.

3.1 Optimized Geometries and Binding Energies of CO_2 Complexes

In this section the binding affinity of CO_2 with all onium ions including methylated onium ions and more importantly with aromatic and heteroaromatic systems is discussed. Figure 1 provides the most energetically favorable structures obtained for CO_2 complexes binding with π systems and onium ions at M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) level of theory. The results obtained indicate that the onium ions bind strongly with the CO_2 as compared to the π systems and binding energies decrease with the increase in the number of methyl groups in onium ion (Figure 2). The trend in binding strength of CO_2···onium ions complexes is as follows O > N > S > P which is in accordance to their electronegativity. In majority of onium ion complexes the X-H (X = N, O and S)···O (CO_2) hydrogen bonding is dominant and this aspect is further elaborated in the discussion on QTAIM analysis. As expected N3, O3 and S3 complexes with CO_2 possess X···O (CO_2) interaction. **S1C** however is stabilized by S···O (CO_2) interaction. In phosphonium ion complexes all complexes are stabilized through P···O (CO_2) interaction.

In the case of π systems, R and F prefer to bind as Lewis acid and Lewis base type interaction where as other π systems are stabilized by π stacking interactions with CO_2. Among all the CO_2··· π complexes, **RC** is the most stable complex with binding energy of 5.09 kcal/mol followed by **ZC** (4.09 kcal/mol) and **UC** (3.60 kcal/mol), **FC** (3.17 kcal/mol), **TC** (3.03 kcal/mol), **BC** (2.73 kcal/mol) and **QC** (2.64 kcal/mol). **RC** and **FC** form CO_2···σ complexes due to the higher polarizing ability of N and O. In all complexes insertion of hetero atom in the five and six member ring greatly enhances the binding with CO_2 either in π stacking or acid base type of interaction. The average difference between BSSE corrected and uncorrected binding energy values for not only the CO_2 complexes but all the complexes analyzed in our study is less than 1.0 kcal/mol.

3.2 Optimized Geometries and Binding Energies of Ammonium Ion Complexes

This is the most commonly observed onium ion in biological systems, especially in proteins, where the cationic ammonium ion of several amino acids is stabilized by cation-π interaction with the aromatic amino acids. The binding energies of 34 ammonium, methylated ammonium ion complexes reported in Table 1 and Figure 3 are the lowest energy structures stabilized by cation-π and CH-π interactions. Complexes formed between N0, N1 and N2 onium ions interacting with π systems are stabilized by the NH-π interactions wherein two hydrogen atoms of onium ion point towards the π system except in case of **QN0** and **RN2**. With the exception of **RN3** all the other N3 complexes show one hydrogen atom pointing towards π system. All N4-π complexes are stabilized by CH-π interactions. As can be observed from Figure 3, **RN4** alone however is stabilized by N···N interaction. Importantly, the binding energy of the onium ion···π complexes decreases with an incremental addition of each methyl group in $H_{(4-n)}Me_nN^+$ (Table 1).

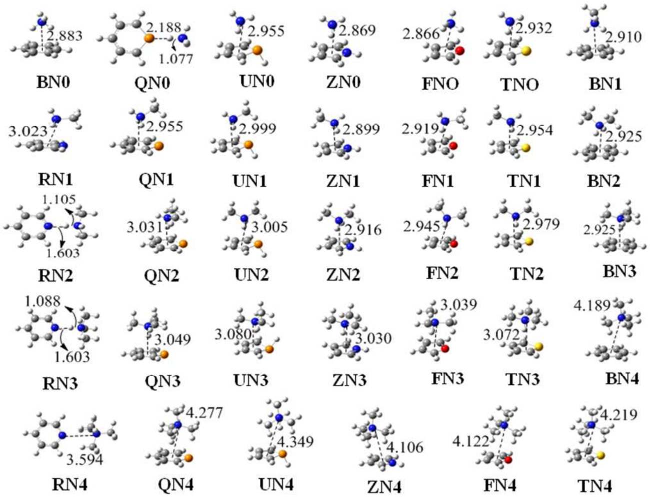

Fig. 3 Geometrical parameters (distances in Å) of ammonium ion complexes computed at M06-2X/6-31G(d) level of theory.

The insertion of hetero atom O, P and S in the five and six membered aromatic ring systems decreases the binding energy compared to the B complexes. On the contrary, the nitrogen containing π systems, R and Z possess higher binding energies than those of the B complexes. Among all the ammonium ion complexes, F has least binding energies while R possesses highest binding energies.

Table 1 Binding energies (BE^a) and BSSE corrected (BE^b) binding energies of ammonium ion complexes computed at M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) level of theory. All energies are in kcal/mol.

π	N0		N1		N2		N3		N4	
	BE^a	BE^b	BE^a	BE^b	BE^a	BE^b	BE^a	BE^b	BE^a	BE^b
B	19.76	19.32	18.58	18.03	17.67	17.04	17.81	16.98	10.44	9.86
R	PT		15.36	14.89	26.24	25.63	24.62	23.94	14.43	13.97
Q	17.55	17.36	16.88	16.29	16.28	15.54	16.21	15.30	9.65	9.00
U	18.20	17.77	17.14	16.60	16.28	15.67	15.88	14.92	10.40	9.80
Z	22.85*	22.44	21.49	20.97	19.99	19.39	19.35	18.63	12.57	12.06
F	16.71	16.30	15.73	15.17	14.67	14.06	14.28	13.52	8.49	7.88
T	18.73	18.17	17.40	16.74	16.68	15.93	16.51	15.57	9.76	9.02

*Not minima on the potential energy surface. PT=Proton transfer complex

The decreasing order of the onium ion binding energy with all π systems is R > Z > B > T > U > Q > F. There are however a few complexes which are low energy structures but are not stabilized by cation-π interaction. These complexes **QN0**, **RN2**, **RN3** and **RN4** having binding energies of 17.36, 25.63, 23.94 and 13.97 kcal/mol (Table 1) are stabilized by NH···P, NH···N, NH···N and N···N interaction (Figure 3) respectively. In case of R these complexes are more stable than the corresponding cation-π complexes. Coming to the case of the proton transfer complexes, **RN0-PT** and **RN1-PT** with binding energies of 23.41kcal/mol and 27.40 kcal/mol respectively are more stable than the cation-π complexes. Although the **ZN$_0$** complex is strongly stabilized by a binding energy of 22.44 kcal/mol it is however not a minima on the potential energy surface.

Table 2 Binding energies (BE^a) and BSSE corrected (BE^b) binding energies of proton transfer complexes computed at M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) level of theory. All energies are in kcal/mol.

Complex	BE^a	BE^b	Complex	BE^a	BE^b
RN0-PT	24.62	23.41	**UO1-PT**	14.03	13.21
RN1-PT	28.47	27.40	**RO2-PT**	19.56	18.69
RP0-PT	12.14	11.54	**RS0-PT**	10.95	10.26
RP1-PT	15.50	14.94	**US0-PT**	8.27	7.48
RO0-PT	18.68	17.55	**ZS0-PT**	7.96	7.27
QO0-PT	14.62	13.79	**RS1-PT**	13.85	13.29
UO0-PT	13.16	12.28	**US1-PT**	9.37	8.79
ZO0-PT	12.82	11.97	**RS2-PT**	16.22	15.67
RO1-PT	20.26	19.28			

Interestingly the R complexes with N0 are stabilized via proton transfer, with N1 by cation-π interaction and with N2, N3 and N4 by NH···N and/or N···N interaction.

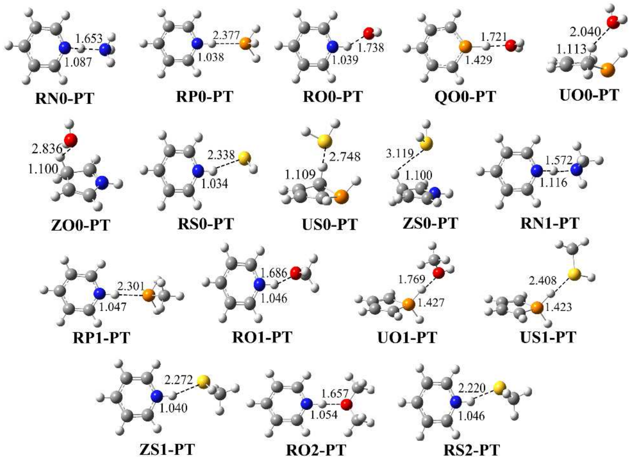

Fig. 4 Geometrical parameters (distances in Å) of proton transfer complexes computed at M06-2X/6-31G(d) level of theory.

3.3 Optimized Geometries and Binding Energies of Phosphonium Ion Complexes

Although phosphorus containing onium ions are less observed in biological systems, their recent application in organic[63] and selected biological systems[58-63] has motivated us to explore their binding mechanisms. Similar to nitrogen containing onium ion complexes we have analyzed the interaction of methylated and nonmethylated phosphorus containing onium ions with aromatic and heteroaromatic systems in 35 complexes. By and large phosphonium ion complexes have less binding energy (Table 3) than the corresponding ammonium ion complexes with the exception of **RP1**, **QP4** and **FP4**. This suggests the P-H bonds are less polar than the N-H bond. Similarly in proton transfer complexes **RP0-PT** and **RP1-PT**, the binding energies are lesser than the corresponding ammonium ion complexes (Table 2). Phosphorus containing onium ions of **BP0** and **ZP0** are not minima on the potential energy surface. The binding mechanism of phosphonium ions with π system is also different from that of the ammonium ions as evidenced by their optimized geometries (Figure 5).

Table 3 Binding energies (BE^a) and BSSE corrected (BE^b) binding energies of phosphonium ion complexes computed at M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) level of theory. All energies are in kcal/mol.

π	P0		P1		P2		P3		P4	
	BE^a	BE^b	BE^a	BE^b	BE^a	BE^b	BE^a	BE^b	BE^a	BE^b
B	17.44*	16.92	15.85	15.12	14.73	13.84	13.30	12.40	10.03	9.27
R	26.38	25.65	21.78	20.72	18.79	17.96	16.57	15.86	14.37	13.66
Q	15.65	15.16	14.37	13.70	13.70	12.83	12.33	11.47	9.85	9.09
U	15.95	15.36	15.11	14.46	14.08	13.24	11.40	10.41	10.39	9.58
Z	20.80*	20.28	18.71	18.02	17.17	16.34	15.40	14.55	12.35	11.65
F	14.39	13.95	13.55	12.86	12.77	11.90	11.67	10.76	9.22	8.30
T	16.51	15.95	14.86	14.09	13.70	12.73	12.44	11.45	9.42	8.48

*Not minima on the potential energy surface.

Unlike, the N0, N1 and N2 complexes which are stabilized by two hydrogen atoms pointing towards π system, the P0, P1, P2 and P3 are stabilized by one hydrogen atom of onium ion pointing towards π system. Incidentally the R phosphonium ion complexes also shown in Figure 5 are all stabilized by N···P electrostatic interactions and have the highest binding energies in case of phosphonium ion complexes. The P4 onium ion complexes are stabilized by multiple CH-π interactions. Similar to the ammonium ions binding with π systems, the decreasing order of the binding energy of phosphonium ions with all π system is also R > Z > B > T > U > Q > F.

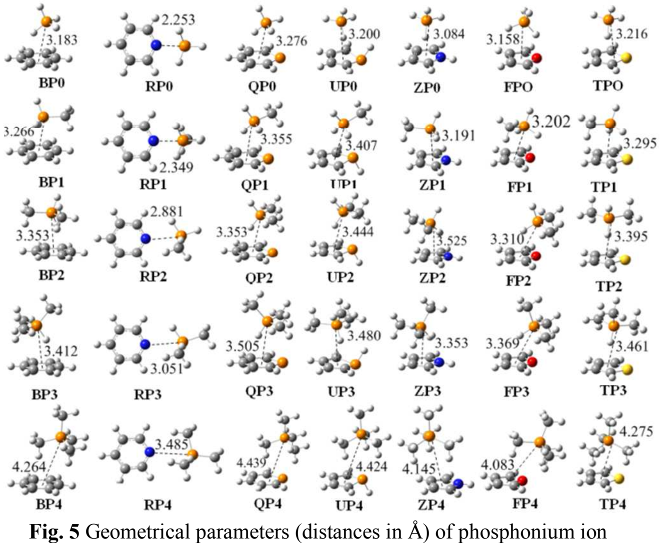

Fig. 5 Geometrical parameters (distances in Å) of phosphonium ion complexes computed at M06-2X/6-31G(d) level of theory.

The nitrogen containing heteroaromatic systems R and Z are more capable of forming complexes with phosphonium ions than the other heteroaromatic systems as reflected in their binding energies observed in Table 3. The incremental addition of methyl group in phosphonium ions also results in an associated decrease in the binding energy of the corresponding complexes. Besides, the cation-π bond distances also typically increase with the increase in the number of methyl groups. For instance the complexes of **BP0** and **BP4** the bond distances increases from 3.183 Å to 4.264 Å with decrease in the binding energy from 16.92 kcal/mol to 9.27 kcal/mol. Moreover, **RP0** and **RP1** shown in Table 3 and Figure 5 and stabilized by N···P interaction are energetically more stable compared to corresponding proton transfer complexes **RP0-PT** and **RP1-PT**.

3.4 Optimized Geometries and Binding Energies of Hydronium Ion Complexes

Due to the high electronegativity of oxygen the O-H bonds are acidic and easily polarizable making them potential candidates for cation-π interactions. A majority of the hydronium ions studied (27 complexes), form comparatively stronger complexes than the other onium ions as reflected in their binding energies (Table 4). Considering hydronium ion-π complexes the distance between the heteroatom of cation and centre of aromatic ring are typically in between 2.70 Å to 3.00 Å except for **QO3** and **ZO3** where it is 4.183 Å and 3.970 Å respectively (Figure 6). In hydronium ion complexes also two hydrogen atoms pointing towards π system form the most stable structures although N···O interactions are also observed in **RO3** complex. Importantly, the binding energies for hydronium ion-π complexes also uniformly decrease with the addition of methyl group in the hydronium ion. **FO0**, **QO1**, **FO1**, **QO2** and **FO2** complexes are stabilized by interaction of hydrogen of onium ion and heteroatom of the ring system.

Table 4 Binding energies (BE^a) and BSSE corrected (BE^b) binding energies of hydronium ion complexes computed at M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) level of theory. All energies are in kcal/mol.

π	O0		O1		O2		O3	
	BE^a	BE^b	BE^a	BE^b	BE^a	BE^b	BE^a	BE^b
B	25.12	24.43	24.19	23.48	22.12	21.31	12.26	11.32
R	20.81	20.20	19.34	18.67	17.67	16.90	16.14	15.65
Q	24.95	24.17	25.98	25.53	22.92	22.44	11.26	10.68
U	25.83	25.25	23.89	22.98	23.70	22.98	13.05	12.12
Z	PT		29.57	28.86	26.77	26.00	14.06	13.52
F	31.88	30.74	24.49	23.55	21.08	20.15	10.64	9.72
T	27.67	26.93	23.75	22.89	21.60	20.63	11.82	10.83

PT=Proton transfer complex

There are 7 proton transfer complexes found with regard to hydronium ion-π complexes, these are **RO0-PT**, **QO0-PT**, **UO0-PT**, **ZO0-PT**, **RO1-PT**, **UO1-PT** and **RO2-PT** with binding energies of 17.55 kcal/mol, 13.79 kcal/mol, 12.28 kcal/mol, 11.97 kcal/mol, 19.28 kcal/mol, 13.21 kcal/mol and 18.69 kcal/mol respectively as shown in Table 2 and Figure 4. Similar to the case of ammonium and phosphonium ions, complexes formed by interaction of hydronium ions with aromatic systems having nitrogen have higher binding energies than the other hetero atom containing aromatic systems. The six membered R is relatively electron deficient ring and is capable of formation of salt with acidic protons and undergoing proton transfer. Three proton transfer complexes **RO0-PT**, **RO1-PT** and **RO2-PT** observed are formed as a consequence of the basic nitrogen atom of R. Highly reactive Z is susceptible for electrophilic substitution reactions at γ position fulfilling the condition upon complex formation with hydronium ions. The **ZO0-PT** exclusively stabilizes proton transfer reaction at γ and the other hydronium ions, O1 and O2 are stabilized by OH-π interactions whereas CH-π interactions are operative in O3 onium ion complex.

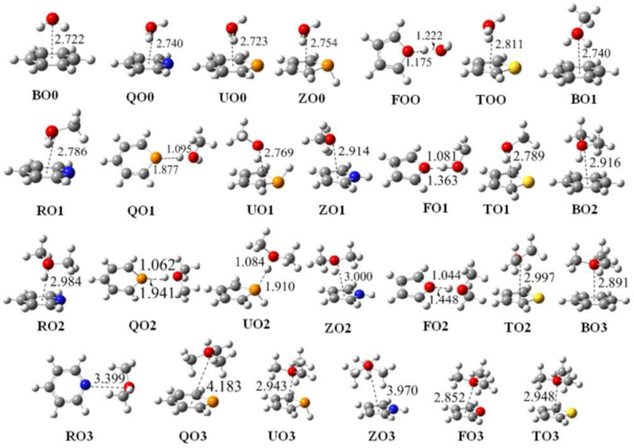

Fig. 6 Geometrical parameters (distances in Å) of hydronium ion complexes computed at M06-2X/6-31G(d) level of theory.

3.5 Optimized Geometries and Binding Energies of Sulfonium Ion Complexes

Sulfur containing onium ions are geometrically and energetically similar to the oxygen containing onium ions. Table 5 shows the trends in binding energies of 27 sulfonium complexes. In sulfonium···π complexes of S0, S1 and S2 stabilized by cation-π interaction two hydrogen atoms point towards the aromatic ring.

Table 5 Binding energies (BE^a) and BSSE corrected (BE^b) binding energies of sulfonium ion complexes computed at M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) level of theory. All energies are in kcal/mol.

π	S0		S1		S2		S3	
	BE^a	BE^b	BE^a	BE^b	BE^a	BE^b	BE^a	BE^b
B	20.89	20.05	18.82	17.86	16.54	15.56	12.01	11.09
R	24.75	24.02	21.70	20.87	19.65	18.59	16.94	16.05
Q	18.85	18.05	17.13	16.19	14.48	13.79	11.41	10.54
U	19.80	18.96	17.44	16.48	16.09	15.07	11.95	10.97
Z	PT		22.71	21.83	20.61	19.62	14.43	13.54
F	19.25	18.43	12.10	11.24	14.35	13.40	11.19	10.19
T	20.41	19.45	17.83	16.88	16.02	14.94	11.36	10.36

PT=Proton transfer complex

The trend in binding energy of sulfonium ions towards π system is R > Z > B > T > U > Q > F similar to that of ammonium and phosphonium complexes. Due to the bulky size of the sulfur atom, bond distances are much higher compared to the case of oxygen containing onium ions. The bond distances increases and binding energies decreases with the substitution of methyl group in the sulfonium ion (Figure 7). These results suggest that the sulfonium ions have weak cation-π interaction in comparison to the oxygen containing onium ions which in turn suggest that the S-H bond is less polar than the O-H bond. In all sulphonium···π complexes the bond distance are found to be more than 3.0 Å suggesting that sulfonium ions prefer to form cation-π complexes rather than proton transfer complexes. Specifically all **RS0**, **RS1**, **RS2** and **RS3** complexes are stabilized by N···S interactions. Moreover, S3 onium complexes are stabilized by CH-π and S···π interactions.

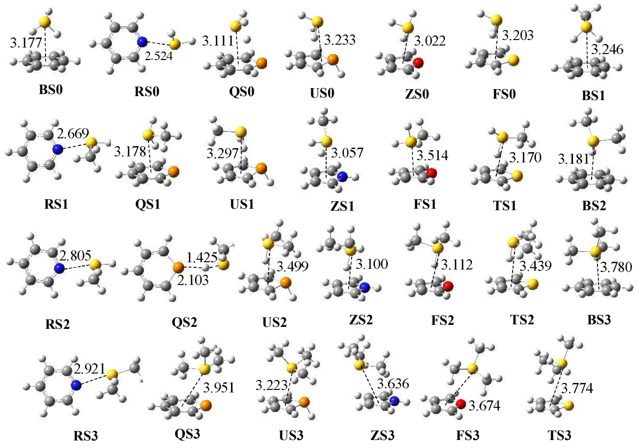

Fig. 7 Geometrical parameters (distances in Å) of sulfonium ion complexes computed at M06-2X/6-31G(d) level of theory.

Interestingly **QS2** is stabilized through a SH···P interaction with a binding energy 13.79 kcal/mol. As can be noted from Table 2, Z exclusively forms proton transfer complex **ZS0-PT** (BE^b = 7.27 kcal/mol) on binding with S0. **RS0-PT**, **RS1-PT** and **RS2-PT** complexes also undergo proton transfer possessing binding energies of 10.26 kcal/mol, 13.29 kcal/mol and 15.67 kcal/mol respectively. Apart from this, **US0-PT** and **US1-PT** also undergo proton transfer.

3.6 Optimized Geometries and Binding Energies of Proton Transfer Complexes

As mentioned individually in the earlier results section 17 systems stabilized by proton transfer have been reported in Table 2 and their principal geometries shown in Figure 4. These complexes have arisen primarily on account of transfer of a proton from less basic system, here typically from onium ions to the more basic hetero atoms containing aromatic system. The binding energies obtained for these complexes are from the interaction of system receiving hydrogen and the hetero atom of onium ion providing the proton. The proton transfer takes place at different positions of heteroaromatic systems. For R the proton abstraction is at nitrogen atom which is known to be more basic and readily available to take proton. Similarly for Q also the proton transfers to the phosphorus atom. U, a five membered system takes proton at β position in **UN0** and **US0** but in **UO1** and **US1** the proton transfer takes place at phosphorus atom of the ring. However, in five member aromatic system Z, which is more reactive towards Electrophilic Substitution Reaction (ESR) compared to F and T, the proton transfer occurs at γ position of the ring.

4. Discussion

4.1 Charge Analysis

The variation in the binding energies and associated charge transfer based on the NPA for CO_2 and ammonium ion complexes computed at M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) level of theory is plotted in Figure 8. Corresponding plots for phosphonium, hydronium and sulfonium ion complexes are available in the supporting information (Figure S6). In CO_2 complexes binding with the π systems, the charge transfer occurs from π systems to CO_2 except in UC, small amount (0.0003) is transferred from CO_2 to U. Especially in the case of nitrogen containing π systems, R and Z a much higher amount of charge transfer (0.0133, 0.0052 a.u. respectively) is observed, while for all other systems the CT is < 0.005.

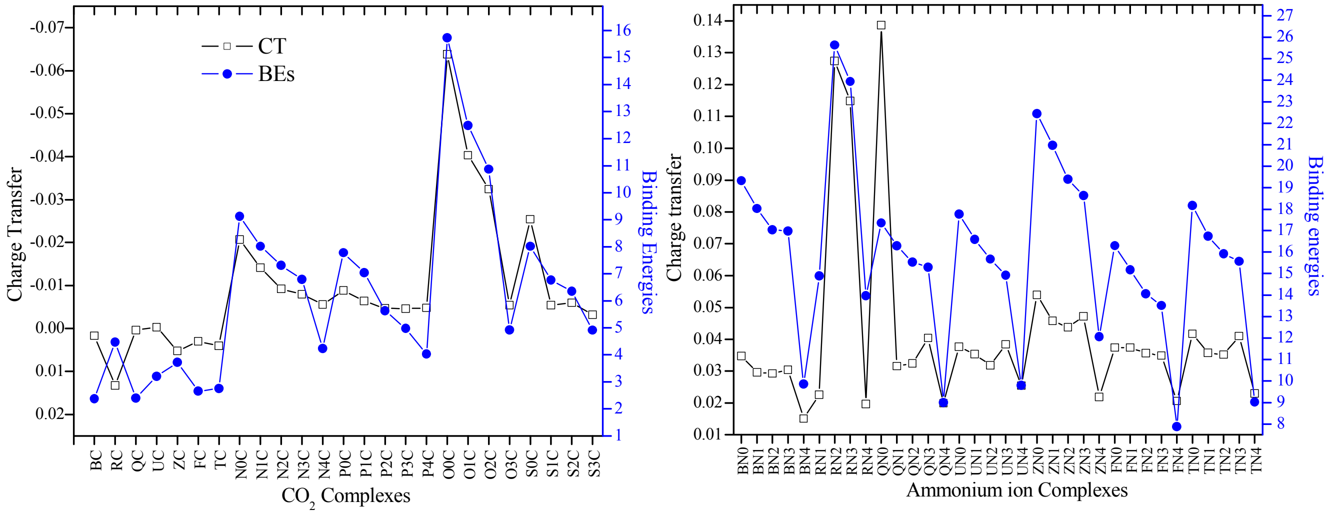

Fig. 8 Variation of the binding energies (BE in kcal/mol) and NPA charge transfer (in a.u) of CO_2 and ammonium ion complexes computed at M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) level of theory. (Blue: Binding energy and Black: Charge transfer)

In case of the entire phosphonium ion···CO_2 complexes, the interaction is primarily between, phosphorus of onium ion and the oxygen of CO_2. The lack of correlation between decreasing binding energies and the near uniform values of charge transfer observed may be attributed to this P(onium)···O(CO_2) interaction. In N4 and S3 complexes with CO_2, the trend of decrease in CT with a decrease in binding energy is not observed.

4.2 QTAIM Analysis

In order to characterize the nature of the noncovalent interactions, QTAIM analysis has been done for all the structures and the topologies of the complexes consistent with the Poincaré-Hopf relationship.[104] In general, satisfying the Poincaré-Hopf equality is considered as an authentication of reliability and completeness of the characteristic set.[105] For a non periodic system such as an isolated molecule or molecular complex the Poincaré-Hopf relationship is calculated as shown in equation 6.

$$n - b + r - c = 1 \quad (6)$$

Where, n stands for number of nuclear critical points denoted with a rank and signature of (3,–3), b for the number of bond critical points (3,–1), r for the number of ring critical points (3,+1), and c for the number of cage critical points (3,+3). Since, the density is generated from a single-point calculation at M06-2X/6-311++G(d,p) level of theory, (3,–1) CPs on the atomic interaction lines (AILs) are reported to characterize the binding between studied monomers. Calculated topological properties (in a.u.) at the (3,-1) CPs of various CO_2 and onium ions complexes obtained at M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) level of theory are reported in Tables S1-S5. Besides, the molecular topology graphs of all complexes studied are provided in Figures S1-S5. The calculated Electron densities ρ(r) and Laplacian of electron density $\nabla^2\rho(r)$ at the (3,–1) critical points including local kinetic energy density G(r), local potential energy density V(r), and local electron energy density H(r) are used to summarize the nature of the bonding interaction. There is a relation[106,107] between these energetic characteristics, that is shown in equation 7.

$$H(r) = G(r) + V(r) \quad (7)$$

Which is also known from the virial theorem that

$$\frac{1}{4}\nabla^2\rho(r) = 2G(r) + V(r) \quad (8)$$

The nature of the interaction can be understood by the ratio, −G(r)/V(r). Based on QTAIM theory, if this ratio is greater than 1 then the nature of the interaction is purely noncovalent,[108] whereas if it falls in between 0.5 and 1 then there exists some degree of covalent character (partial covalent character)[108,109] and where −G(r)/V(r) is less than 0.5, it is a shared interaction.[108] The balance between those two values (G(r) and V(r)) determines the kind of interaction. In general, negative and positive values of $\nabla^2\rho(r)$ represent the covalent[110] and noncovalent[111] interactions (van der Waals interactions and H-bonds) respectively.

It can be seen for the CO_2 and onium ion complexes at (3,–1) CPs, the ratio of the kinetic electron energy density G(r) and the potential electron energy density V(r) is greater than one which indicate that the nature of the interaction is purely noncovalent. Exception to this is seen in some complexes where the ratio is in between 0.5 and 1, indicating that these interactions have partial covalent character. This is observed in case of CO_2 (**O0C** and **O1C**), ammonium ion (**RN2**, **RN3** and **QN0**), phosphonium ion (**RP0** and **RP1**), hydronium ion (**QO2**, **UO1**, **ZO1**, **ZO2**, **FO1**, **FO2**, **TO0** and **TO2**) and in sulfonium ions (**RS0**, **QS0**, **QS2**, **US2**, **ZS1**, **ZS2** and **FS0**). The hydronium ion complexes, **QO1**, **UO2** and **FO0** have –G(r)/V(r) less than 0.5 and show negative $\nabla^2\rho(r)$ further confirming the existence of covalent interaction between the two systems.[108,112] Further in all the other system studied herein, H(r) values are positive and –G(r)/V(r) is greater than 1 indicative of noncovalent interactions. For the hydrogen bonded complexes, which are mentioned above as exceptional cases, the positive laplacian values indicate that the interaction is mainly electrostatic, while the fact that –G(r)/V(r) is in between 0.5 and 1 suggests that it is also partly covalent, as corroborated by the negative H(r) values at the considered CP.[107,113]

The hydrogen bond interactions between oxygen atoms of CO_2 and acidic hydrogen of onium ions are strongly dominant in total binding strength as compared to the π systems. Electron densities (ρ(r)) and Laplacian of electron density ($\nabla^2\rho(r)$) at (3,–1) CPs between CO_2 and onium ions are in the range of hydrogen bond interactions (~0.02 a.u.).[114] As the number of methyl substituents increase, as expected multiple atomic interactions with the oxygen atom of CO_2 ensue, but all these are very weak as seen in terms of their electron densities and ratio between G(r) and V(r) at their corresponding (3,–1) CPs. π systems binding with CO_2 are stabilized due to π-π interaction and for the specific cases of RC and FC strong Lewis acid base kind of interaction is found to stabilize the complex. A high ρ(r) value has been seen at (3,–1) CPs between two monomers and as the number of methyl substituents increase, the number of atomic interaction lines increases with low density at the (3,–1) CP of the corresponding atomic interaction lines.

4.3 LMO-EDA Analysis

To provide insights into the contributions of different components of binding energy of complexes studied, a scheme developed by Su and Li popularly known as the LMO-EDA was employed. LMO-EDA is an energy decomposition analysis scheme for interactions in gas phase with HF or KS orbitals. Decomposing the total interaction energy into electrostatic, exchange, repulsion, polarization, and dispersion interaction terms, the LMO-EDA method is able to investigate nonbonding and bonding interactions with closed or open shell systems. The advantage of LMO-EDA is that EDA can be performed with DFT methods like M06-2X also.

The $CO_2\cdots\pi$ complexes are primarily stabilized due to the dispersion term followed by contributions from electrostatic and polarization components. As was visualized by their binding energies in $CO_2\cdots\sigma$ complexes **RC** and **FC**, electrostatic term has a significant role in stabilization of complex especially in **RC**. Besides, the exchange and polarization term contribute equally to the binding energy of **RC** complex. In all other $CO_2\cdots\pi$ complexes, the contribution of the polarization term is higher than the exchange component (Figure 9). In CO_2 complexes with onium ions, electrostatic and polarization components are the primary contributors to the stability of N0, N1, N2, N3, P0, P1, P2, O0, O1, O2, S1and S2 complexes. This may be attributed to the hydrogen bonding interactions observed between the polar hydrogen atom of onium ion and the highly electro negative oxygen atom of CO_2. Dispersion plays a key role in methylated N4, P2, P3, P4, O3 and S3 complexes either by CH···O(CO_2) interaction and/or by N···O(CO_2), P···O(CO_2) and S···O(CO_2) interaction.

In general for onium ion complexes with π systems, the electrostatic and polarization terms primarily contribute to the interaction in the complex (Figure 9 and Figure S7). As the number of methyl groups increases the dispersion term is seen to have a key role in stabilization of complex. This can be appreciated in the light of a recent study by Grimme and Schreiner[115] on tertiary butyl groups which provide overall positive stabilization through attractive dispersion interactions in their system. In case of ammonium ion complexes, different trends were observed while studying its interaction with different aromatic and heteroaromatic systems. The benzene complexes are primarily stabilized by the electrostatic component in N0, N1 and N2 complexes, while N3 and N4 complexes are stabilized due to the dispersion component. N0 complexes of nitrogen containing aromatic systems R and Z are stabilized by electrostatic component whereas dispersion component is dominant in the N1, N2, N3 and N4 complexes. Similarly, N0, N1, N2 complexes of F and T are stabilized by electrostatic component and the remaining N3 and N4 by dispersion component. For N0 complexes of phosphorus containing aromatic systems Q and U, the polarization component is dominant over the electrostatic term and dispersion term. N3 and N4 complexes are stabilized by dispersion component.

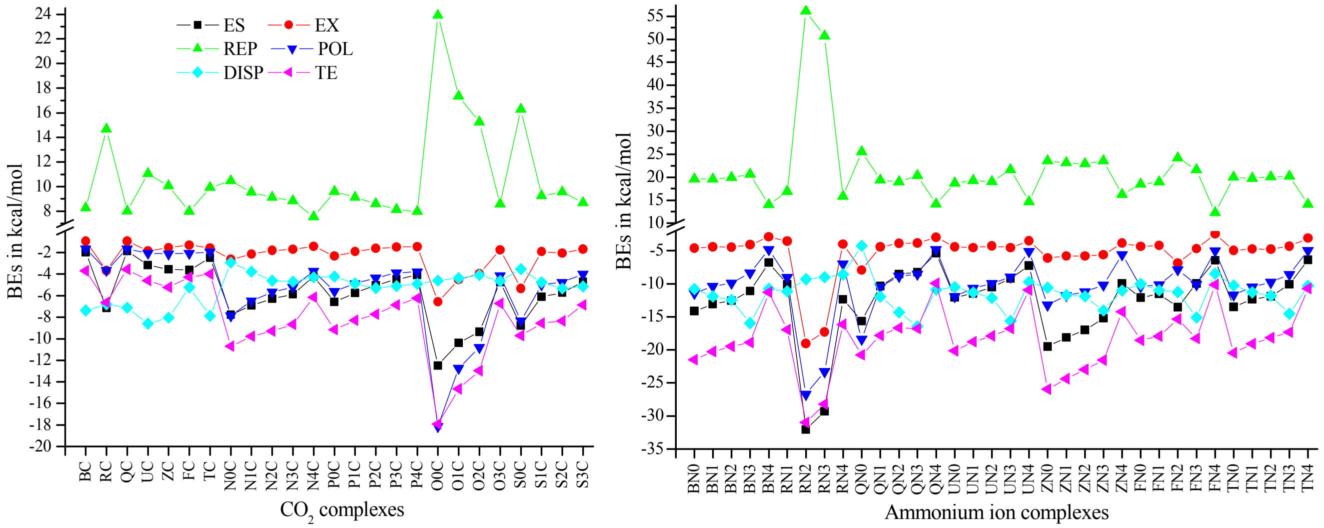

Fig. 9 Contribution of various factors towards the total binding energy as calculated at the M06-2X/6-31G(d) level using the LMO-EDA approach for CO_2 and ammonium ion complexes. (Black: Electrostatic, Red: Exchange, Green: Repulsion, Blue: Polarization, Cyan: Dispersion, Pink: Total Interaction Energy)

Phosphonium ion complexes of B, Q, U, F and T are primarily dominated by dispersion component. R and selected Z complexes (**ZP0**, **ZP1**and **ZP2**) with phosphonium ions owe their stability to contribution from the electrostatic term. **UP0** alone is stabilized by polarization component and the remaining U complexes of P1, P2, P3 and P4 by dispersion component. The complexes of highly electro negative oxygen containing hydronium ions are primarily stabilized by polarization term on binding with aromatic systems. In the lone case of **BO0** primary contribution to stabilization is by electrostatic component. Also in all O3 complexes except **RO3** dispersion component seems to be important. The **RO3** complex is primarily stabilized by electrostatic term which is due to the N···O interaction. In most of the complexes of sulfonium ion polarization term provides major contribution to the binding energy. Similar to hydronium ion complexes all R and some B complexes (**BS0** and **BS1**) are stabilized due to electrostatic term. Besides dispersion component gives a higher contribution to the total binding energy of all S3 complexes.

Thus from the LMO-EDA analysis, it is clear that the nature of the hetero atom in both the aromatic ring and the onium ion plays a vital role in determining the physical character of intermolecular interactions. As is evident from the above discussion the extent of methylation of the onium ions also significantly alters the contributions of different interacting energy components.

4.4 Proton Affinity (PAs) and Methyl Cation Affinity (MCAs)

Proton affinities and methyl cation affinities were computed to explain proton transfer between onium ion and π system (Table 6). From the obtained PA values it is evident that the proton transfers from an onium ion to an aromatic system which has a proton affinity higher than the proton affinity of neutral counterpart (NH_3, PH_3, SH_2 and OH_2) of onium ions (N0, P0, S0 and O0 respectively).

The computed PAs and experimentally available PAs clearly reveal that the aromatic compounds have higher PA values as compared to the PAs of neutral counterpart of onium ions and all the reactions where proton transfer occurs are hence exothermic. For instance, this is seen in proton transfer from N0 (PA = 207.1 kcal/mol) to R (PA = 222.09 kcal/mol) during the complexation. Thus R receives a proton when interacting with N0, N1, P0, P1, O0, O1, O2, S0, S1 and S2. This suggests that pyridine is more basic than these onium ions. Apart from R the other complexes of aromatic systems which are involved in proton transfer are **QO0**, **UO0**, **ZO0**, **UO1**, **US0**, **ZS0** and **US1**. The proton transfer occurs also at α, β and γ carbons of the hetero cyclic ring in the complex formation with few onium ions. The PAs at α, β and γ positions of aromatic compounds is higher than the PAs of the NH_3, PH_3, SH_2 and OH_2. In five membered heterocyclic compounds proton transfer takes place from onium ion to α, β and γ carbons of the hetero cyclic ring which indicates that these positions are susceptible to bind with a proton.

Table 6. Computed proton affinities (PAs), methyl cation affinities (MCAs) and available experimental proton affinities for all parent systems computed at M06-2X/6-31G(d) level. All values are in kcal/mol.

S. No	Compound	PAs	MCAs	Expt. PAs[#]	Reference
1	NH_3	207.1	118.7	204.0	99
2	NH_2Me	214.9	122.0	214.9	99
3	$NHMe_2$	222.2	128.3	222.2	99
4	NMe_3	226.2	136.9	226.8	99
5	PH_3	184.4	108.7	188.0	99
6	PH_2Me	200.6	119.4	203.5	99
7	$PHMe_2$	213.3	132.1	218.0	99
8	PMe_3	223.8	145.3	229.2	99
9	OH_2	168.4	80.9	165.0	99
10	OHMe	180.9	87.3	180.3	99
11	OMe_2	187.6	98.2	189.0	99
12	SH_2	164.7	85.2	168.0	99
13	SHMe	180.0	95.7	184.8	99
14	SMe_2	193.2	111.8	198.6	99
15	C_6H_6	180.6	88.0	179.3	99
16	C_5H_5N	222.1	132.6	222.0	99
17	C_5H_5P	192.9	114.1	195.4	99
18	C_4H_5N	209.7	99.9	209.2	99
19	C_4H_4O	195.1	109.0	192.0	99
20	C_4H_4S	195.1	89.6	194.8	99
21	C_4H_5P	218.3	141.2	201.6	116

[#] Proton affinities of bases were determined absolutely or derived from the procedure described in corresponding reference at temperature 298 K.

5. Conclusions

Our study provides a systematic analysis of increasing methyl substitution on the onium ions in CO_2 and aromatic complexes. Clearly, the heteroatom substitution in the aromatic ring also plays a significant role in binding mechanism. Heteroatom substitution in these complexes results in multiple X···π (X=N, P, O and S), NH-π, PH-π, OH-π, SH-π, CH-π, π-π, hydrogen bonding and/or dispersion interactions. Apart from CO_2···π complexes seen in B, Q, U, F and T, binding with highly electronegative oxygen and nitrogen atoms in R and Z aromatic systems leads to σ-bonding. Hydrogen bonding is observed in CO_2 binding with onium ions. The nature of the hetero atom also plays a significant role in both cation-π and proton transfer complexes. Out of the 17 proton transfer complexes only in the case of U and Z a proton transfer to the aromatic carbon is observed.

In CO_2 complexes, NPA helps to establish flow of charge from CO_2 to onium ions and from aromatic systems to CO_2. Further, in onium ions binding with aromatic systems, charge flow from aromatic system to onium ions is noted. The QTAIM analysis reveals the hydrogen bond interactions between CO_2 and onium ions and weak dispersion forces in aromatic systems. From the LMO-EDA analysis, it is clear that the nature of the hetero atom in both the aromatic ring and the onium ion plays a vital role in determining the physical character of intermolecular interactions. As is evident from the discussion section the extent of methylation of the onium ions also significantly alters the contributions of different interacting energy components especially dispersion. A linear correlation is observed for the experimental and computed PA and MCA data. Thus the study serves as a step towards the development of bioinspired systems to capture CO_2 through a quantitative evaluation of CO_2 binding with small model systems. Our study provides a comprehensive understanding of binding mechanism of methylated/nonmethylated N, P, O and S containing onium ions with aromatic systems.

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