UNHINDERED TRIANGULENE SALT PAIRS: SUBSTITUTION-DEPENDENT CONTACT ION PAIRING AND COMPLEX SOLVENT-SEPARATED DISCOTIC IONS IN SOLUTION

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UNHINDERED TRIANGULENE SALT PAIRS: SUBSTITUTION-DEPENDENT CONTACT ION PAIRING AND COMPLEX SOLVENT-SEPARATED DISCOTIC IONS IN SOLUTION

DISSertation

A dissertation submitted in partial fulfillment of the requirement for the degree of Doctor of Philosophy in the College of Arts and Science at the University of Kentucky

By

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Lexington, Kentucky

Director: Dr. Arthur Cammers, Professor of Chemistry
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2015

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ABSTRACT OF DISSERTATION

UNHINDERED TRIANGULENE SALT PAIRS: SUBSTITUTION-DEPENDENT CONTACT ION PAIRING AND COMPLEX SOLVENT-SEPARATED DISCOTIC IONS IN SOLUTION

This work sought to enforce aromatic interactions between compatible $\pi$-molecular orbital systems with ionic bonding. In this case the interacting partners are oppositely charged discotic triangulene derivatives. The observed properties of the heterodimERIC ion-pairs likely arise due to a hypothetical synergy between electrostatics and $\pi$-interactions. The work presented here describes investigation of putative covalency arising from this hypothetical synergy in the electrostatics driven $\pi$-stacking. In order to probe this, various hypotheses were made and experiments were designed to test their validity. The results from the experiments show existence of contact ion-pairs and complex solvent-separated discotic ions in solution. The formation of complex ion-pairs arise due to the fact that the electrostatic interaction that brings the discotic ions together is strong, but does not neutralize when the contact is made. So, the dipole created by the monopoles in a dimeric contact ion-pair can attract ions at both termini forming oligomers. This process apparently continues towards highly aggregated states and then to nanometric species and at some point the material precipitates. The propensity to aggregate and form complex-ions limited our approach to the measurement of the energetics of the ion-pairing for two reasons: (1) the observables had a complex dependence on temperature, solvent, concentration and ionic strength; and (2) the mass in solution was undergoing kinetic evolution towards solid states. The turbidimetric effects arising due to aggregate formation further complicated the extraction of weak interactions between the ions and hence effects determination of ion-pairing constants.

Keywords: triangulenes, pancake bonding, $\pi$-stacking, ion-pairing

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05/04/2015
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To my family...
ACKNOWLEDGEMENTS

I deem it my honor to write this section of the document, as the work presented here would not have been possible without individual contributions from various people… At the outset, I would like to thank my advisor, Dr. Arthur Cammers, who has put in a lot of effort in various capacities, scientific or otherwise, to transform the immature individual in me into a student of science. His constant guidance during my graduate career has helped me to improve my thinking critically and scientifically. I remember my first meeting with him when he encouraged me to think ‘beyond’ - this is still in progress.

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Chapter 1
Introduction

1.1 Aim of the Work

This study sought to enforce interactions between aromatic molecules with compatible $\pi$-molecular orbitals (MO). In this case the two aromatic monomers interacting are oppositely charged. So, Coulomb’s law primarily should govern their close approach and cohesive energy. A secondary effect however could be possible if the aromatic faces can get close enough for bonding interactions to occur between the discotic pairs. Evidence for face-to-face bonding has been presented in the chemical literature for a wide variety of discotic interactions: radical-radical,\textsuperscript{1-11} anion-anion,\textsuperscript{12-17} cation-anion.\textsuperscript{18-20} The experimental observations have been framed by theoretical models for covalent contributions to the bonding.\textsuperscript{21-28} The experimentation in the present work revolves around the following objectives: (1) to design ionic molecular complexes that enhance face-to-face bonding, (2) to test if this interaction between the monopoles has a covalent component or if it is only electrostatics, (3) to assess the interaction as a function of symmetrical and symmetry-breaking atomic substitution.

Reader’s guide:

The following sections give some background related to the present work in the context of non-covalent interactions, in particular chemical literature on efforts to understand various contributions to aromatic interactions.\textsuperscript{29-99} Readers informed about aromatic interactions might pay some attention to section 1.3 on pancake bonding. The current work sought to investigate the phenomenon of pancake bonding, in which some level of covalent interaction contributes to the interaction between aromatic faces. Readers informed about pancake bonds might skip to section 1.4 in which the specific arguments and the molecules under study are introduced.
1.2 Background

Molecular interactions can be broadly described into two types: covalent and noncovalent. The covalent interaction is characterized by differential electron transfer from one atomic or molecular species to another in the process of bonding resulting in the formation of a new molecule. The noncovalent interactions have various sub-classes: van der Waals (dispersion) interactions (favorable temporal fluctuations at the (µ-wave frequency)⁻¹ timescale), dipolar / quadrupolar interactions (favorable directional intermolecular interactions between electrostatic molecular moments), hydrophobic interactions and electrostatic interactions (Coulombic interaction between oppositely charged species). The result of noncovalent interactions is the formation of a molecular assembly with properties distinct from the freely solvated monomeric species. As the extent of noncovalent interaction increases, the properties of the aggregate become progressively less like the individual molecules in terms of solubility and spectroscopic signatures. However, the noncovalent interactions are considerably weaker than the covalent interactions, except in the case of ionic association, which is a comparatively strong interaction.

Despite evidence for covalent character in special cases of π-interaction, interactions between aromatic rings are usually characterized as chimeric interactions, basically dispersive interactions. These *electrodynamic* interactions are comparatively weak in the absence of electrostatic (quadrupole, dipole, monopole) interactions. The gossamer nature of the aromatic interaction is a common occurrence with small aromatic hydrocarbons like benzene, naphthalene, where they are found to have similar interaction energies as compared to the corresponding saturated hydrocarbons. In fused polycyclic aromatic hydrocarbons, with increased number of delocalized π-electrons, the π-π interactions seem to have greater attractive forces. The directional nature of these weak interactions has its origin in various molecular level descriptions.27,28,38,100

π-stacking is often conceived as an interaction between aromatic compounds where an energetically important geometry with maximum interaction is possible. For
strong π-π stacking interactions to occur, the most suitable arrangements have been shown to be the ones in which the donor and the acceptor molecules lie above each other with their molecular planes being mostly parallel, like a Cₙ-symmetrical molecule; an outcome of Mulliken’s maximum overlap condition. The examples of such parallel-stacked geometry are not commonly observed in chemical, biological or supramolecular systems. Interestingly, many experimental and theoretical chemists have considered polarization of π-systems to describe interactions in aromatic molecules. Hunter and Sanders have provided a qualitative polar/π-model that served as the starting point for predicting geometries in aromatic interactions. This model was one of the many views that supported T-shaped or parallel-displaced arrangements being the predominant geometry in aromatic interactions. These arrangements yield favorable attractive interactions between the π-electrons and the σ-framework that overcome the π-repulsions as in face-to-face center-to-center arrangement. These CH-π interactions seem to provide a global energy minimum among the possible arrangements. Quite interestingly, the same model predicts quadrupolar driven face-to-face center-to-center stacking between electron-rich aromatics and electron-poor aromatics. The sandwich geometry in these electron donor-acceptor (EDA) type complexes provides maximum orbital overlap. A variety of attempts have been made to measure and quantify the extent of interaction and stabilization that could be obtained when two neutral aromatics with opposite quadrupole moments approach each other in a face-to-face manner.

The electrostatic component of polar/π scenario has been extended to design intramolecular π-interactions between aromatic moieties. In these cases, it has been observed that favorable interactions can result when at least one of the interacting aromatic moieties is electron-deficient. In one such example, intramolecular stacking of electron poor pyridinium cation with aryl group has been demonstrated in the solid state of conformationally restricted π-stacked pyridinium systems and also in liquid state NMR and fluorescence studies of conformationally flexible pyridinium systems. A number of model systems with a variety of spectroscopic methods have been demonstrated to explore inter- and intramolecular stacking interactions. Such
stacking interactions were not observed when both the interacting aromatics were electron-rich or electron-deficient.\textsuperscript{121-123}

Cammers’ research group investigated synergistic effects of electrostatics and weak aromatic interactions in solution and crystalline state. Initial studies revealed importance of charge in intramolecular association of aromatic molecules.\textsuperscript{124} Clear evidences were found that showed preferential folding to attain aromatic association between the $\pi$-faces of central phenyl ring and the pyridyl ring in conformationally flexible charged m-xylylene derivatives (Figure 1.1). The isostructural neutral analogues preferred an unfolded conformation. This study, along with many others found in literature,\textsuperscript{28,125-128} emphasized the need of an electron deficient $\pi$ system in order to observe stronger aromatic association, like in the case of cation-$\pi$ interaction, than any neutral $\pi$-$\pi$ interaction. Curiously, the anion-$\pi$ interaction seems to have conflicting conclusions.\textsuperscript{14,15,17,129-134} This is probably due to putative repulsion between two electron-rich moieties. The overall interaction seems to be mainly due to the electrostatic attractions with some contribution arising from the anion-induced polarization of the electron-deficient aromatic moiety.\textsuperscript{14,17,135} This was evidenced in the theoretical study of halide ion binding with hexafluorobenzene where the most electronegative fluoride ions showed greatest affinity.\textsuperscript{14}

![Figure 1.1](image_url)

\textbf{Figure 1.1 Structures of neutral and charged m-xylylene derivatives used as molecular templates in the conformational analysis.}

Further studies in Cammers group evaluated the effect of charge when it was part of the interacting system. Since the requirement of electron deficient systems and the role of charge for better aromatic association have been established, studying association between electron rich and electron poor systems, with charge as part of both the systems, would provide evidence to the role of ionic electrostatics in aromatic association.
Discotic aromatic triangulene derivatives containing positive and negative charges were used to maximize the Coulombic contribution to aromatic association. In the presence of strong electrostatic attractions, any observable indicating aromatic association should be enhanced.

1.3 Pancake Bonding

In the context of bonding described between π-stacks in radical dimers (Figure 1.3), *pancake bond*\textsuperscript{136,137} finds a special mention. Pancake bonding interactions are related to π-stacking interactions, however the contact distances observed here are much shorter than the van der Waal distances. These are mostly referred to as π-dimers because the intradimer C-C bonding is mainly due to the overlap of the π* orbitals at the central sp\textsuperscript{2} hybridized carbon atoms. The bonding system prefers an orientation that allows maximum multicenter overlap (2e-mc).\textsuperscript{138,139} The preference arises due to the energetic gain obtained by lowering of the energy of the singly occupied molecular orbital (SOMO) of the radical upon overlap with the neighbor (Figure 1.2). The resulting bonding HOMO is doubly occupied.

![Figure 1.2 MO diagram for pancake bonded dimers.](image)

\(\pi\)-dimers (Figure 1.3) of this type arise when the unpaired radicals are sufficiently close to each other. Stable electron transfer salts are formed when radical cations or radical anions approach near bonding distances but avoid bonding due to strong Coulombic repulsions. Long, multicenter bonding is used to describe the structure and observed electronic and magnetic properties in the case of radical salts dimers.\textsuperscript{2,3,12,140} The long bond descriptions have also been used to describe bonding in some neutral radical dimers, eg. TBPLY.\textsuperscript{141-144} In these cases the stability of the dimeric association
has other contributors (electrostatic cation-anion, dispersion) in addition to stabilization from SOMO-SOMO overlap.

The role of SOMO-SOMO overlap between a radical dimer has been studied in the light of $\pi^*-\pi^*$ overlap in TCNE. There are at least a few key aspects of this bonding interaction that can put this interaction as categorically different from other intermolecular interactions. These are:

a) the monomers are doublets, while the resulting dimers are singlets.
b) the preferred configuration is an outcome of the net stabilization upon direct overlap of SOMO that is sensitive to the phases of the interacting SOMO’s.
c) HOMO-LUMO electronic transition in the resulting complex shifts to a lower energy.
d) the bonding energies are significantly smaller than that of normal chemical bond but larger than a $\pi$-stack dimer.
e) the resulting bond is significantly shorter than the van der Waal distance.

![Diagram of molecular structures](image)

**Figure 1.3 Examples of pancake bonded dimers.**

The intermolecular bond lengths are typically shorter than the sum of the van der Waal radii. The shortest predicted value is 2.74 Å but the shortest that has been observed so far is 2.80 Å. The prototypical persistent TCNE anion radical dimer has been studied in a great detail due to the sub van der Waals intermolecular distance reported in the $\pi$-dimer. The solid-state motif of the anion radical is described in terms of $\sigma$-dimer with long $\sigma$-bond (Figure 1.4 (a)) having an intermolecular distance...
D=1.61 Å and two π-dimer arrangements (Figure 1.4 (b, c)). In the π-dimer (Figure 1.4 (b)) with an intermolecular separation D=3.47 Å, one of the TCNE molecules has a longitudinal offset along the molecular axis relative to other. This offset is not observed in the other π-dimer (Figure 1.4 (c)) with face-to-face overlap at a separation D=2.90 Å, a distance shorter than the van der Waal but longer than C-C bond.

![Figure 1.4 Bonding in TCNE anion radical.](image)

Motivation to investigate π-stacking pancake interaction arises in the pursuit to make molecular materials with high electrical conductivity\textsuperscript{148} and for spintronics.\textsuperscript{149} It is also useful for the understanding electrical and magnetic properties of π-radical aggregate derived organic conductors.\textsuperscript{150-152}

The complexes such as 1•2 (described below) in the present study are related to pancake bonding between π-aromatic faces. In terms of Mulliken,\textsuperscript{153} these donor-acceptor complexes can be considered as loose 1:1 molecular compounds that can be quantum mechanically described as

\[
\psi_N \approx a\psi_0(D,A) + b\psi_1(D^+-A^-)
\]

where the wave functions \(\psi_0(D,A)\) represents a no-bond structure and \(\psi_0(D^+-A^-)\) a dative structure for the donor-acceptor pair D, A.
**Figure 1.5 MO diagram of 1•2 showing interaction of HOMO of 2 with LUMO of 1.**

The interaction between doubly occupied HOMO of 2 with the LUMO of 1 (Figure 1.5) in the case of molecular complexes 1•2 satisfies the definition of a bond, which Pauling describes as the force between a group of atoms that are such as to lead to an aggregate with sufficient stability to make it convenient for the chemist to consider it as an independent molecular species.\(^{154}\)

### 1.4 Is there any covalency in electrostatic driven \(\pi\)-stacking?

Strong covalent and weak non-covalent interactions have very different origins. When two atoms interact by overlap of orbitals, the bond formed by sharing of electrons is a covalent bond. The bond formed is generally short, about 1.5 Å. Such overlap of orbitals is not required for non-covalent interactions and so these are long distance interactions. Since there is no direct interaction necessary for non-covalent interactions to occur, the reason for the interactions lies in the fundamental electronic nature of the interacting systems. The origin of non-covalent interactions can be due to interactions between permanent dipoles (electrostatic), a dipole and an induced dipole (induction) and between an induced dipole and another induced dipole (dispersion). The overall stabilization gained by a system with non-covalent interactions is less than about 25 kcal/mol, when compared to about 50-200 kcal/mol bond energy of a covalent bond. So in summary, the bond dipole in Scheme 1.1 can vanish (as in the case of identical atomic groups) or can decrease beyond the pure electrostatic limit with covalent interaction. Likewise the energy of the interaction can decrease beyond the electrostatic limit given increasing covalent character in the interaction.
Scheme 1.1 A Schematic depiction of the difference between ionic (top) and covalent (bottom) bonding. The association of monopoles produces a dipole with a dipole moment (μ) (solid line in the graph) but in the covalent line (dashed line in graph) μ can drop to zero with attendant small changes in interatomic distance (r).

If the covalent contribution to aromatic interactions is significant, it should be discoverable in the following set of triangulene derivatives (Figure 1.6):

Figure 1.6 Structures of triangulene cations and anion used in the study.

In this dissertation, cation, represented by 1, refers to the triangulene derivatives with aromatic core containing a unit positive charge. Anion, represented by 2, refers to the triangulene derivative with aromatic core containing a unit negative charge. The
smaller ions, BF$_4^-$ and NBu$_4^+$ present for charge balance, are of less interest. 1•2 is the heterodimeric salt pair.

1.5 Molecular Orbital Calculations

Triangulene hydrocarbons, also called as Clar’s hydrocarbon$^{155}$, are non-Kekulé aromatic hydrocarbons, with the parent triangulene having an aromatic biradical description (Figure 1.7). Many cationic and some anionic triangulene derivatives have been synthesized that are stable because in the cation the empty orbital is non-bonding and in the anion the occupied orbital is non-bonding. In the derivatives discussed herein, the cationic LUMO and the anionic HOMO are isosymmetric. The fundamental reason for this can be grasped from an appreciation of basic Hückel theory.

![Figure 1.7 The parent biradical triangulene hydrocarbon; a non-Kekulé even alternant hydrocarbon](image)

To gain insight into the electronic nature of the charged triangulene derivatives in Figure 1.6, molecular orbital (MO) calculations were utilized. The basic MOs of the triangulene derivatives were obtained from Hückel molecular orbital calculations. The MOs with electronic arrangement are shown in Figure 1.8. Although Hückel MO calculations are crude by modern computational standards, it is interesting to note that the MO symmetries of the \( \pi \)-systems are reflected in higher-level calculations. These MO analyses of the \( \pi \)-framework of the triangulene derivatives indicate that the LUMO of the cation 1 and the HOMO of the anion 2 should bear the same symmetry label. And since the HOMO of 2 and LUMO of 1 is essentially the same MO (Figure 1.9), a high degree of MO interaction might be expected between the HOMO of the electron-donating 2 and LUMO of the electron-accepting 1.
Figure 1.8 SHMO calculations showing Hückel energy diagram of anionic 2(O)\textsubscript{3}, and cationic 1(NH)\textsubscript{3}.

![Energy Diagram](image)

Figure 1.9 rhf/6-31g calculations showing the A\textsubscript{1g} orbitals of (a) cationic 1(NH)\textsubscript{3} (LUMO) and (b) anionic 2(O)\textsubscript{3} (HOMO).

![Orbitals](image)

At the rhf/6-31g level of theory the LUMO energy levels appear to vary almost linearly as a function of the number of N atoms in the triangulenium discotic (Figure 1.10). If the interaction between oppositely charged discotics can be rudimentarily described as a Lewis acid/ base reaction, one might suppose that 1(O)\textsubscript{3}•2(O)\textsubscript{3} should have the strongest interaction and the ionic interaction in 1(NMe)\textsubscript{3}•2(O)\textsubscript{3} should be the weakest interaction in the set of aza-oxa salts from trioxa to trimethyltriaza.
On the other hand, if symmetry breakage were more important to the energy of the interaction between 1 and 2, a profile like the one in Figure 1.11 would be expected. Figure 1.11 graphs the energy gap between HOMO and LUMO of the cation 1. In this case the $D_{3h}$ triangulenium molecules $(1(O)_3$ and $1(NH)_3$) bear two degenerate HOMOs. These energy-level differ in the $C_{2v}$ triangulenium molecules $(1(O)(NH)_2$ and $1(O)_2(NH))$. While the result of symmetry breakage on the energy of the interaction might not be the same as the breakage in the degeneracy of the HOMO orbitals, the effects of symmetry breakage in the ionic interactions should be borne in mind before evidence may indicate that they can safely be ignored. The effect of symmetry is certainly not evident in the $A_{1g}$ orbitals in the series: $1(O)_3$, $1(O)_2(NH)$, $1(O)(NH)_2$ and $1(NH)_3$. This orbital appears to be identical for all intents across the substitution series.
Figure 1.11 rhf/6-31g energy gap between of the LUMO and the HOMO orbitals in $1(O)_3$ to $1(NH)_3$ as a function of the number of N atoms (n) in the discotic.

1.6 Hypotheses

We wanted to investigate if there is any covalency in the electrostatics driven aromatic interactions between cation $1$ and anion $2$. To approach this, we formulated some working hypothesis and tested them with experimentation.

1.6.1 The interaction energy ($E_{ip}$) as a function of electronic symmetry may indicate covalency

When the oppositely charged discotics $1$ and $2$ interact, the heterodimeric species $1\cdot2$ produced will be a neutral ion pair. Optimal contact between $1$ and $2$ due to high compatibility of interacting MOs would be expected if there were any covalency in the aromatic interaction. In such a case the symmetry of the MO should affect the degree of covalency in the interaction. But if there is no covalency present in the aromatic interaction, then the ion pairing between $1$ and $2$ should be purely based on electrostatic attractions. In such a case the substitution pattern, changing from $1(O)_3$, $1(O)_2(NMe)$, $1(O)(NMe)_2$ and $1(NMe)_3$ should have very little effect on the energy of ion-pairing interaction (Figure 1.12, dotted line). If there is any covalency in bonding, the symmetrical cations $1(O)_3$ and $1(NMe)_3$ should have a higher degree of interaction with $2(O)_3$ than the dissymmetrical cations $1(O)_2(NMe)$ or $1(O)(NMe)_2$. Hence the energy of ion-pairing will be higher when dissymmetrical cations, $1(O)_2(NMe)$ and $1(O)(NMe)_2$, interact with $2(O)_3$ as compared to the symmetrical cations $1(O)_3$ and $1(NMe)_3$ (Figure
There should also be a difference in the equilibrium constant for the ion pairs $1(O)_3 \cdot 2(O)_3$ and $1(NMe)_3 \cdot 2(O)_3$ if there is a covalent aspect to the interaction between 1 and 2, in addition to electrostatics.

Figure 1.12 Hypothetical dependence of ion-pairing energy of non-encumbered cations with anion as a function of symmetry; when covalency part of aromatic interaction (dashed) and in the absence of covalency (dotted).

1.6.2 Energy of ion-pairing ($E_{ip}$) will depend on the reduction potential of the cation

If there is a covalent component to the electrostatic driven interaction between 1 and 2, it should be evidenced during the measurements of redox potentials. If a covalent bond forms, its bond strength should be a function of the reduction potential of the Lewis acid 1. The electronegativity differences between oxygen and nitrogen will give rise to differences with respect to the electrophilicity or Lewis acidity among the cations $1(O)_3$, $1(O)_2(NMe)$, $1(O)(NMe)_2$, and $1(NMe)_3$.

The reduction potential of an ion is its ability to be reduced by electron acceptance. Consequently, $1(O)_3$ should have the highest reduction potential among the cations under consideration due to the presence of three relatively more electronegative O atoms. The reduction potential of $1(NMe)_3$ should be the lowest among the cations being considered and it has been demonstrated that $1(O)_3$ is a better electron acceptor than $1(NMe)_3$.\textsuperscript{156,157} Now since $1(O)_3$ is a better electron acceptor, in its association with $2(O)_3$, the ion-pairing should be lower in energy than the interaction between $1(NMe)_3$.
and $2(O)_3$. The mixed derivatives, $1(O)_2(NMe)$ and $1(O)(NMe)_2$ should follow the intermediate trend (Figure 1.13).

![Figure 1.13](image)

**Figure 1.13** Hypothetical dependence of ion-pairing energy of non-encumbered cations with anion as a function of reduction potential of cation if covalent interaction contributes to ion-pairing.

### 1.6.3 Shift in oxidation potential of $2(O)_3$ is a measure of $E_{ip}$

If there is any contact in the interaction between 1 and 2, then there will be a positive shift the oxidation potential upon ion-pairing compared to the oxidation potential of “free” $2(O)_3$. This is because the “bound” species will be increasingly difficult to oxidize. The extent of the interaction can be then correlated with the $E_{ip}$ determined by UV-Vis experiments.

### 1.7 Role of sterics at the edges

Based on the type of substitution at the edges, the triangulene cations used in this study can be broadly classified into two groups: (1) the non-encumbered cations where the substitution is either O or NMe; and (2) the sterically encumbered cations with at least one angular group (-CH$_2$- unit) as the substituent at the alkyl side chain on N. Molecular measurements usually do not show great differences with Me- or Et-substitutions. But in the case of triangulene salt pairs of the type 1•2 even such a difference showed major variations in the properties of salt pairs. In the crystalline state studies of the 1(NEt)$_3$, it has been observed that the cation packed as a polymer of face-
to-face staggered dimer. The side chains of one of the cation pointed above the aromatic plane and the side chains of another cation of the stacking dimer has its side chains pointed below the aromatic plane. The ethyl substitution at the edge should provide an energetic benchmark if this group can be confined to one side of the disc and is not free to rotate.

In the absence of any covalent component in the aromatic interaction, the major contribution to ion pairing would be due to electrostatics. So, the ion pairing measurements would be almost equal with aromatic salts formed by non-encumbered cations 1(O)₃, 1(O)₂(NMe), 1(O)(NMe)₂ and 1(NMe)₃. In addition, any difference in the measurements between the encumbered and non-encumbered derivatives should originate due to steric interactions that are brought about by the angular substituent. These differences should be evidenced in the ion pairs formed by 1(O)(NMe)(NEt), 1(O)(NEt)₂, 1(O)₂(NEt) and 1(NEt)₃.

1.8 Overview of the results

π-stacking is theorized to have a strong electrostatic contribution. The charged triangulene derivatives used in this study would be expected to maximize this electrostatic contribution to π-stacking. During investigation of association between various aromatic triangulene cations and anion, the observations indicated likely operation of synergism between stronger electrostatic interactions and weaker π-interactions. It is noteworthy that this effect is evident only in aromatics that present no steric encumbrance to the face-to-face interaction. The integration seems to have some covalent component as favorable interactions were observed when the molecules approached bonding near covalent distances. The following section is an overview of the observations noted during our quest for covalency in interactions between aromatic ions. Based on the evidences from previous studies, in terms of the role of substitution, the compounds were designed that could increase facial contact between the aromatic ions. Careful choice of conditions for the study was necessary as we were looking at very weak interactions that would be complicated by solvent interventions.
1.8.1 Spectrophotometric approach

We expected to study the equilibrium for the heterodimeric ion-pairing by monitoring the evolution or disappearance of the signature absorbance bands by UV-Vis.

**Scheme 1.2 Formation of heterodimeric ion-pair, 1•2, from oppositely charged triangulene cations, 1, and triangulene anion, 2(O)₃.**

The equilibrium shown above (Scheme 1.2) would have been easy to study and quantify by standard solution state UV-Vis measurements. As will be discussed later, the association of 1 and 2 produces long-wavelength absorbance band in the regions where neither 1 nor 2 have any absorbance. So, if this observable related to the concentration of 1•2, the equilibrium constant for the ion-pairing could be extracted by following classical treatment of the data.

So if, $1 + 2 \rightleftharpoons 1 \cdot 2$  \hspace{1cm} (2)

then the equilibrium constant for the ion-pairing can be given by

$$K_{ip} = \frac{[1 \cdot 2]}{[1][2]}$$  \hspace{1cm} (3)

or,

$$[1 \cdot 2] = K_{ip}[1][2]$$  \hspace{1cm} (4)

However all observations lead to the conclusion that the nature of the ion-pairing is likely more complex (Scheme 1.3) due to the presence of higher order aggregates in addition to heterodimeric 1•2. Some questions to answer were if the species present in the solution is
a simple 1:1 contact or loose ion-pair \(1\cdot2\). Are there any indications for the presence of trimeric species \(1\cdot2\cdot1\) and \(2\cdot1\cdot2\) or other oligomeric /polymeric \((1\cdot2)_n\)?

\[
\begin{align*}
\text{Scheme 1.3 Complex ion-pairing in triangulene monopoles; red represents the discotic cation and the blue represents discotic anion.}
\end{align*}
\]

1.8.2 Electrochemical approach

Electrochemical measurements should also provide useful information about the nature of the interactions between these charged aromatic systems. Redox processes are measurements of the energetics of the process of electron removal and electron donation of a given system. These processes should be occurring from the most accessible MOs, i.e. HOMO and LUMO. So, we can derive energies of these MOs from the redox potentials. The oxidation potential could be related to the ionization potential of the molecule, as this is the process of removal of electron that occurs from the HOMO of the molecule. Similarly, the reduction potential should be indicative of the electron affinity of the molecule involving adding an electron to the LUMO of the molecule.

We expected to measure the energetics of the ion-pair formation by comparing the redox potentials of the “free” species (cation and anion with non-aromatic counter ions) with the redox potentials of the ion-pairs (in the presence of oppositely charged aromatic counter). Some questions to answer were: how would the oxidation potential of \(2(\text{O}_3)\cdot\text{NBu}_4\) change in the presence of \(1\cdot\text{BF}_4\) when measured in the same solvent? Would
the change in oxidation potential be same irrespective of the nature of 1•BF₄? How much shift in the reduction potential would be observed with 1•2 vs. 1•BF₄?

The HOMO of 1•2 has resemblance from the HOMO of 2 and the LUMO has the characteristics from the LUMO of 1. So, the redox potential measurements for 1•2 can be compared to those for 1•BF₄ and 2(O₃)•NBu₄. Any gain in stability due to the formation of 1•2 should be evident in these comparative measurements. The oxidation potential of 1•2 would reflect the energy of the HOMO of the ion-pair. The shift in the oxidation potential of the ion-pairs in the series 1(O)₃, 1(O)₂(NMe), 1(O)(NMe)₂ and 1(NMe)₃ from the oxidation potential of 2(O₃)•NBu₄ would reflect the energy of the HOMO of the ion-pairs as a function of heteroatomic substitution on the discotic cations. If the aromatic interactions are mainly electrostatic driven, then there should be only small variations in the oxidation potentials among the non-encumbered ion-pairs. But if there is any covalent component to the aromatic interaction 1•2, we should see substantial perturbation to the oxidation potential among these ion-pairs. Free energy measurements should be indicative of these variations and direct evidence to covalency.

As bond strength is a measure of reduction potential of the Lewis acid, more electrophilic cation 1, will have better association with 2. We should also be able to see if the alkyl substitution at the edges would have any effect on the oxidation potential of 1•2 when compared with 2(O₃)•NBu₄.

From the results that were obtained during our investigation, we could definitely see the effect of electrostatically driven aromatic interactions. There might be some covalency in this phenomenon, but these were experimentally difficult to evaluate quantitatively, as the exact nature of speciation in the solution state was difficult to extract. The experimental results were complex as they were greatly affected by aggregation causing turbidimetric effects that muddled the determination of association constants.

1.9 Overview of the impact of the findings

The solubility limitations of the compounds under study and almost instantaneous nature of formation of aggregating ion-pairs upon mixing of 1 and 2 constrained
application of any of the solution state methods in the determination of ion-pairing equilibrium constant. Attempts to overcome these limitations via varying temperature, ionic strength etc. remained unsuccessful as the ion-pairs were trapped kinetically as aggregated nanometric species. So a comprehensive comparison of ion-pairing, in the non-encumbered salts, as a function of atomic substitution on the cation could not be carried out.

Although our studies were not quantitative and are largely inconclusive of the nature of species causing the observed effects, the work challenges previous work on weak interactions and the interpretation of the nature of aromatic cation or anion ion-pairs in solution.\textsuperscript{159-162} As Mulliken noted,\textsuperscript{163} in stable 1:1 complexes, a donor-acceptor interaction must also involve site saturation in addition to saturation in charge-transfer attraction. So with both donor and acceptor having π-faces, which can have favorable interactions from top and bottom sides of π-face, complexes of type 1:2 (2•1•2) or 2:1 (1•2•1) might be expected and the extreme end would be a columnar stack with alternate arrangement of donor and acceptor (-1•2-)\textsubscript{n}. The triangulene ions under study might represent this extreme. This picture of a columnar stack can be envisaged from the calculations of electrostatic potential of 1(O\textsubscript{3})•2(O\textsubscript{3}). Even though there is a strong attractive interaction due to hard electrostatics between the oppositely charged discotics, the glue bringing the two discs together is not completely neutralized in the heterodimer upon contact. The cationic face of the dimer (Figure 1.14(a)) still bears a residual positive electrostatic potential and the anionic face still bears a residual negative electrostatic potential (Figure 1.14(b)). The resulting dipole can favorably attract oppositely charged monopoles at both the termini (side view Figure 1.14(c)). Based on this we can imagine a polymeric arrangement with alternating cationic and anionic discs in the case of salt pairs. Crystalline state studies of available 1•2 salt pairs reflect this arrangement. Curiously similar polymeric arrangement is also observed with various cations 1 but not with anion 2(O\textsubscript{3}).
Figure 1.14 Electrostatic potential map of 1(O₃)•2(O₃) showing cationic, anionic and side face view.

The observations of the present work puts forth strong question as to why all the aromatic donor-acceptor interactions observed before should not be more complicated than a 1:1 interaction. In the absence of covalent component, the discotics should equilibrate between free species and paired species. When the covalent component exists and without any steric hindrance between the molecules, the ion pairs can form complex oligomeric or polymeric species (Figure 1.15).

Figure 1.15 Pictorial representation of formation of complex cationic (left) and anionic trimeric (right) species

The formation of trimeric species should be a complex function of the steric destabilization of the central ion in the trimeric species being formed. If this aspect is to be questioned then we can argue for the very small differences between ions with 1(O)₃ or 1(NMe)₃ as the central ion. In that case we would expect to see preferences for cationic or anionic trimers. A small steric destabilization could possibly be seen in that case when 1(NMe)₃ is the central ion. This would also be the case with the mixed derivatives 1(O)₂(NMe) and 1(O)(NMe)₂. With almost no steric interactions at the edges, 1(O)₃
would not have much preference for cationic (1•2•1) or anionic (2•1•2) trimers, but the
greater electrophilic nature of 1(O)₃ might prefer an anionic trimer (2•1•2).

The chapters to follow will discuss in detail the experiments for the synthesis of
various candidates and the solution state methods that were used to test the hypothetical
covalent nature of electrostatic driven aromatic interactions.
Chapter 2
Complex Solution State Ion-pairing in Triangulene Salts

This chapter is an effort to unveil complex solution state phenomenon observed in the study of ion-pair \(1 \cdot 2\). Evidence will be presented that will hopefully demonstrate ion-pairing that is more complicated than a simple 1:1 pair defined by heterodimerization of 1 and 2. A detailed account of the experiments involved in the study of binding event will be discussed at a later stage of the dissertation, however, observations selected from various experiments will be woven together to give a glimpse of electrostatically driven solution state, non-covalent interaction in aromatic triangulene salts. While an in depth analysis probing into the extent of aggregation and its solvent-, concentration- and temperature-dependence is in order, observations from some of the experiments will substantiate our understanding of the complex nature of association.

2.1 Important terms related to the work

Before going into the experimental details and the discussion of results, the key terms pertinent to the work are defined below.

2.1.1 Ion-pairing

At an elementary level, an ion pair can be defined as a pair of oppositely charged ions held together by Coulomb’s force of attraction without covalent bonding. Coulomb’s law explains the interactions between charged particles:

\[
F = \frac{q_1 q_2}{\varepsilon r^2}
\]

where \(F\) is the force of attraction, \(q_1\) and \(q_2\) are the magnitudes of the charges, \(\varepsilon\) is the dielectric constant of the medium and \(r\) is the distance between the ions. So, there is an inverse relation between electrical force between two atoms and the square of the distance separating them.

For a long time ion pairing has commanded special attention in the study of intermolecular interactions in relation to biochemical, macromolecular or even in the study of reaction mechanism.\(^ {164-167}\) Various models have been proposed for ion pair
formation. Fuoss, Sadek\textsuperscript{168-170} and later Grunwald\textsuperscript{171} proposed formation of ion pairs by association of free ions in a stepwise process. Initial formation of ion pair may include one or both ions with their solvation shells.\textsuperscript{168,172-174} As the ions come closer, some energy will be required to achieve partial desolvation of ions. The driving force for the formation of contact ion pair comes from increased Coulombic attraction and gain in the entropy due to desolvation.\textsuperscript{169,171} Grunwald represented the types of ion pairs by potential energy minima determined by the interionic distance between the ions in the pair.

2.1.2 Types of ion-pairs

Depending on the relative geometric arrangements of the interacting ions and the solvent molecules in the solution, various types of ion-pairs have been described. According to the IUPAC nomenclature,\textsuperscript{175} an ion-pair in which the constituent ions have a direct contact with no intervening molecules is designated as tight ion pair, symbolically represented as $X^+Y^-$. The resulting tight ion-pair or contact ion-pair are formed by the two ions that are solvated from outside and they appear like a solvated electric dipole (Figure 2.1).

![Figure 2.1 Ion-pairing in solution.](image)

An ion pair in which the constituent ions are separated by at least one solvent molecule is referred to as a loose ion pair, represented by $X^+\parallel Y^-$. A conceptual distinction with respect to the extent of separation of ions in case of loose ion pairs has been made. \textit{Solvent-separated ion-pairs} are formed when two ions with their own primary solvation shells are in contact via overlapping secondary and further solvation shells. \textit{Solvent-shared ion-pairs} have two ions separated by a distance to accommodate
only one solvent molecule. The ions in this case have their own solvation shells that can interpenetrate (Figure 2.1).

A distinction between contact ion-pair and loose ion-pair could possibly be accomplished experimentally. In the loose ion-pair exchange with free ions in solution is readily feasible. Isotopic labeling can be used to achieve this. Due to the penetration of the solvent molecules between the ion-pair couple, significant change in spectral properties of contact and solvent-separated ion-pairs can be easily observed. UV-Vis, ESR and NMR measurements have been used to distinguish between contact and solvent-separated ion-pairs. An unambiguous distinction between solvent-shared and solvent-separated ion pairs, however, is difficult experimentally as even increasing relative permittivity and ion-solvating power of the solvents favor overcoming the energetic barrier that is required to create a void even between two ions of tight ion-pairs for the introduction of solvent molecules. The other extreme would be having free unpaired ions that have their own solvation shells without any influence on the other ions. Marcus and Swarcz have explored conditions in which contact, solvent-shared and solvent-separated ion-pairs in solution can exist as thermodynamically distinct species. Curiously, theoretical calculations of Gibbs free energy profile for the hydrolysis of tert-butyl chloride involving separation of tert-butyl cation from chloride ion support the formation of contact ion-pairs during the reaction. The solvent-shared, solvent-separated and free ions seem to be energetically similar species during the reaction. An energy barrier of about 2 kcal/mol has been calculated between contact and solvent-separated ion pairs.

2.1.3 Complex Ion-pairing

The solution state study of triangulene ion-pairs offered many observations that diverged from the three types described above and a 1:1 ion-pair of the type 1•2 seems insufficient to explain the observations. Complex ion-pairs of the type 1•2•1 and 2•1•2 or oligomeric nanometric species that possibly exist as loose-pair with non-chromophoric BF₄(−) and NBu₄(+) or discotic 1 and 2 counter ions could be involved to produce these effects. Some evidence to the presence of complex ion-pairs came through the work done
in Cammers’ group. This was seen mainly with the association of non-encumbered cations, 1(O)₃ and 1(NMe)₃, with anion 2(O)₃.

2.1.4 Charge Transfer

The nature of organic molecular complexes has been widely studied by chemists and physicists for more than half a century since Mulliken put forward his charge-transfer (CT) theory. His observation of spontaneous coloration of solution of electron-rich donor (D) and electron-deficient acceptor (A) was explained as an occurrence due to the diffusional interaction of D and A to form an encounter EDA complex. According to Mulliken, the excitation of the CT band of a non-bonded EDA complex produces transient radical ion pair.

![Scheme 2.1 Formation of encounter complex by diffusion](image)

This theory was experimentally supported by the study of an EDA complex of 9-cyanoanthracene and tetracyanoethylene (TCNE). When the CT band (630 nm) of this complex was exclusively excited with a Nd³⁺:YAG laser pulse (532 nm), two new transient absorption bands at 770 nm and 440 nm were observed due to formation of TCNE anion radical (440 nm) and CNA cation radical (770 nm). These bands were not due to uncomplexed CNA or TCNE. It was later confirmed that such a photo-induced electron transfer observed in the CNA-TCNE complex by a vertical transition corresponds to a contact ion-pair.

The extent of electron transfer between the donor and acceptor in principle can vary from zero to complete transfer. When neutral molecules undergo complete electron transfer they produce radical-ions. The charge transfer complex thus formed is stabilized by the electrostatics between the two molecules and is a weak electron resonance rather than a covalent or an ionic bond. Excitation of these species frequently occurs at wavelengths longer than the donor and the acceptor and the resulting absorption band is often referred to as charge-transfer bands. Optical and magnetic spectroscopy is a commonly used method to study CT bands.
The study of energetics of CT complexes\textsuperscript{192} shows that the process of complex formation and its energy characteristics depend to a large extent on the ionization potential (IP) of the donor D and the electron affinity (EA) of the acceptor A. So the amount of energy required for the excitation (equation 1) of the CT complex will be

\[
\frac{hc}{\lambda_{\text{CT}}} = I_D - E_A - W
\]

where \( h \) is the Planck’s constant, \( \lambda_{\text{CT}} \) is the wavelength of CT transition, \( I_D \) is the IP of donor, \( E_A \) is the EA of acceptor and \( W \) is the electrostatic energy of the ion pair \([D^+, A^-] \). The energy of formation of CT complexes requires hundreds to thousand calories per mole. The overall energetics of the system will depend upon various other factors that influence the system. For example, the binding of the electron donor and the electron acceptor in CT complexes is not necessarily purely due to charge transfer; other intermolecular forces may also contribute or influence the formation of the complex.\textsuperscript{193}

As mentioned earlier, absorption spectroscopy has been one of the most commonly employed techniques for quantitative evaluation of solution state intermolecular interactions. In this method, the appearance of CT absorption bands at a wavelength different from the absorption of the constituent molecules, arising from the transition between donor and acceptor molecules is easy to detect.\textsuperscript{136,186,189,194} A variety of EDA interactions ranging from highly transient complexes,\textsuperscript{163,195} with collisional lifetimes, to those present as extremely stable and isolable crystalline 1:1 complexes.\textsuperscript{193,196,197} The CT band should be carefully interpreted, as the observation of CT band doesn’t necessarily imply presence of stable CT complex.\textsuperscript{136,163} Contact pairs, molecular pairs that are not bound, can also alter the absorption spectrum including contribution to the CT band. Charge transfer between two molecules that does not produce a bound species is referred to as contact charge transfer.\textsuperscript{163,198} In this case the electron donors and acceptor molecules are randomly distributed in an inert solvent. When these molecules are sufficiently close during a random encounter, a momentary charge transfer takes place which results in a CT absorption. Oxygen is the most common one electron acceptor that does contact charge transfer.\textsuperscript{199} The equilibrium constant measurements for these complexes invariably yields a very low formation constant, about
0 to 1 M$^{-1}$, as the binding energy here is almost negligible, about 3 kJ/mol. Binding energy in stable ground-state CT complexes is significant and the association constant is larger. Some examples of ground-state CT interactions have been observed with fullerenes (C$_{60}$ and C$_{70}$) and aromatic amines like N,N-dimethylaniline and N,N-diethylaniline in various solvents. The measured equilibrium constants were variable depending on the solvents used to study with values between 0.04 and 2.6 M$^{-1}$.

Bhattacharya et al. have reported CT interaction of C$_{70}$ with aromatic hydrocarbons having a high equilibrium constant values between 11 to 490 M$^{-1}$.

In the study of EDA complexes, the interactions between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are most important. A CT band is usually observed when the energy difference between the HOMO of the donor and the LUMO of the acceptor is relatively small. Substitution effects play important role in tuning the energy of MOs. In general, electron-donating groups raise the energy level of the HOMO and electron-withdrawing groups (EWG) lower the energy level of the LUMO; a very commonly used strategy to design materials for electronic and photovoltaic applications.

Although the use of the term CT is common in literature for any observation of absorbance bands at wavelengths (usually longer) other than the constituent molecules, this dissertation does not refer to the long-wavelength absorption bands due to donor-acceptor complex formation as a CT band.

2.2 UV-Vis Absorption Spectroscopy

2.2.1 Investigation of ion-pairing by UV-Vis

UV-Vis spectroscopy is widely used experimental technique to determine binding constants where a significant spectral change occurs due to complexation. Several experiments have been designed to study binding and stoichiometry during a complexation reaction. Among the various methods for determination of stoichiometry, Job’s and Yoe and Jones’ methods are the most widely used due to simpler mathematical and experimental set up involved. It is advisable to have an idea about stoichiometry of the complex before determining the binding constant. A standard method of determining
association constants is by setting up a binding isotherm for the system of interest and fitting the experimental data to the theoretical binding isotherm. A binding isotherm is simply a theoretical change in some observable, for example absorption due to complex in this case, as a function of concentration of the varying component. As the name suggests this should be done at a constant temperature.

An earlier method of determining association constant, developed in Cammers’ group, was based on varying the concentration of an equimolar mix of 1 and 2 by dilution of a solution of higher concentration to get a lower concentration of the mix. A series of equations were set up to evaluate equilibrium constant based on the fraction of unassociated ions assuming 100% 1:1 complexation. Absorbencies due to certain

![Figure 2.2 UV-Vis absorption comparison of 1:1 mixture of four non-encumbered cations 1 and anion 2 (measured, red) with sum of absorptions due to individual 1•BF₄ and 2•NBu₄ (calculated, blue) in propylene carbonate. (a) 1(O)₃ and 2; (b) 1(O)₂(NMe) and 2; (c) 1(O)(NMe)₂ and 2; and (d) 1(NMe)₃ and 2.](image)
concentrations of 1 and same concentration of 2 were subtracted from the absorbance of equal concentration of 1:1 mixture of the two to see if there were any interactions between 1 and 2. The average standard deviations of the ratios of absorptions at different pairs of wavelengths were used to plot against the fraction of unassociated ions obtained by iteratively converging on values to get a self-consistent association constant for different concentrations.

Figure 2.3 UV-Vis absorption comparison of 1:1 mixture of three encumbered cations 1 and anion 2 (measured, red) with sum of absorptions due to individual 1 and 2 (calculated, blue) in propylene carbonate. (a) 1(NEt)₃ and 2; (b) 1(O)(NMe)(NEt) and 2; and (c) 1(O)₂(NEt) and 2.

When equimolar solutions of 1 and 2 are mixed, the UV-Vis absorption profile of the mix (Figure 2.2, measured, red) is significantly different from the linear superposition of the absorptions due to individual constituent ions, 1 and 2 (Figure 2.2, calculated, blue) at the same concentration, in complexes where the cation has no sterics at the
edges. All the four non-encumbered salt pairs showed long-wavelength absorption in the near-IR regions where neither the cation nor the anion alone absorb (Figure 2.2). With the introduction of sterics at the edges of the cation, there is no significant change in the absorption of the mix (Figure 2.3, measured, red) when compared to the linear superposition of the absorptions due to individual constituent ions, (Figure 2.3 calculated, blue). This is because the angular group partially blocks the close approach of another π-face from one side of the discotic (Figure 2.4). This indicates that when non-encumbered 1 and 2 come close together, both of them experience a different electronic environment as a result of ion-pairing. The ion-pairing in this case must be a contact ion-pairing that results in a significant alteration of the UV spectrum upon complexation.

Figure 2.4 Angular groups blocking close approach of π-face.

Compelling arguments can be made in order to partially support our hypothesis (1.6.1) that symmetry of the interacting MO can dictate the extent of covalency in the interaction under study. There are clear differences in the measured and the calculated spectra in figures 2.2 and 2.3 that appear to be the result of symmetry of interacting MOs of the donor and acceptor. As mentioned earlier, MO compatibility ensures better donor-acceptor interaction. The interaction between symmetrical cations 1(O)₃ and 1(NMe)₃ with 2(O)₃ is characterized by noticeable influence on the absorption in the regions where 1 and 2 absorb. The vertical electron transfer process is optimized when the donor and acceptor molecules are perfectly aligned to achieve best possible face-to-face center-to-center stacking arrangement. When the A₁g HOMO of 2(O)₃ interacts with A₁g LUMO of 1(O)₃ or 1(NMe)₃, where both the molecules are D₃h symmetric, the resulting MO still bears near D₃h symmetry. The absorption profile of the complex is quite different from the constituent monopoles. On the other hand, with introduction of symmetry breaking substituents, the interaction between C₂ᵥ symmetric 1(O)(NMe) and 1(O)(NMe)₂
acceptors with D$_{3h}$ donor 2(O)$_3$, results in an offset face-to-face interaction, the extent of which is determined the relative electronegativities of O and N in the mixed aza-oxa derivatives. A hypothetical symmetry-induced offset alignment in the contact ion-pair decreases the difference in UV absorption of the contact ion-pair and UV absorption of the solvent-separated ion pair. This rationalizes the big absorption differences between spectra 2.2(a) and 2.2(d) compared to the smaller absorption differences between spectra 2.2(b) and 2.2(c). The perturbations are most noticeable in the region where anion 2 absorbs (600-700 nm). The interaction in this case chooses energy minima to compensate electrostatic and electronic contributions. The encumbered cations, in addition, present steric components and it was observed that presence of even one angular group could turn the long-wavelength interaction off (Figure 2.3).

Solution state studies of the triangulene salts, especially salts with non-encumbered cations, were largely limited by their low solubility in most of the commonly used organic solvents. Solvents investigated were DMSO (dielectric, $\varepsilon=47.24$), CH$_3$CN ($\varepsilon=36.64$), (CH$_3$)$_2$CO ($\varepsilon=21.01$), CHCl$_3$ ($\varepsilon=4.81$), etc. Screening solvents based on dielectric constant, propylene carbonate (PC, $\varepsilon=64.9$) was picked for ion-pairing studies. It was observed that the cations, anion and the salts had a superior solubility in PC, although it was difficult to keep the salts at relatively high concentration in solution over a long period of time.

A quick look at the UV-Vis spectra of the non-encumbered salts pairs revealed that the long-wavelength absorption phenomenon was substitution dependent (Figure 2.5). It was noted that as the number of aza bridges in the cation increased from zero in 1(O)$_3$ to three in 1(NMe)$_3$, via the mixed derivatives, the long-wavelength absorption band in the complex shows a hypsochromic shift. This change in the long-wavelength absorption band with cation identity suggests operation of effects in addition to electrostatics. Since the long-wavelength absorption band was unique to each of the non-encumbered salt pairs, the UV-Vis experimentation utilized these signature spectral bands for studying ion-pairing.
Figure 2.5 Comparison of UV-vis spectra of salts of four non-encumbered cations (1) with anion (2).

In related fields of study, the CT band absorption has been previously used for quantifying association in many donor-acceptor systems.\textsuperscript{153,163,186,196,219-221} These are mainly interactions involving electron-rich donor molecules with electron-deficient molecules via transfer of a fraction of electronic charge.

In order to quantify the ion-pairing in triangulene salts, we had to choose methods to perturb the equilibrium of ion-pairing that would influence the long-wavelength absorption band. This was approached in the following ways:

1) Change in concentration of the reacting species by dilution or titration methods
2) Changing the temperature
3) Varying the ionic strength of the medium

If the ion-pairing between 1 and 2 were a 1:1 complex, the determination of association constant (ion-pairing constant), $K_{ip}$, by the available methods would have been easier. The thermodynamics of the system, in terms of $\Delta H$, $\Delta S$ and $\Delta G$, also would have been easier to obtain by graphical treatments. However, the presence of higher order aggregates in solution mixtures of 1 and 2 made these determinations far more complicated.
2.2.2 Turbidity and absorbance

In the titration experiments, discussed in detail in chapter 4, it was observed that as the concentration of the ions (1 and 2) increased, the complex formation, characterized by long-wavelength absorption, was accompanied by elevation in the baseline and spectral broadening. This was due to the formation of nanometric species capable of scattering light due to their molecular size approximating the wavelength of the UV light. Turbidity is a direct measure of the concentration of suspended solid particles. The suspension can be due to large molecules of microscopic colloidal particles. The presence of these particles result in the formation of a suspension, which is a heterogeneous system. When the molecules are highly chromophoric, the properties of absorbance and turbidity are similar phenomena. Following Beer’s law, absorbance is directly proportional to the concentration of light absorbing chromophore. Turbidity can be measured by obtaining absorbance or scattering of a system. Turbidity is more complicated and it does not follow Beer’s law. Turbidity is dependent on both number and size of the particles in a suspension. In order to know the size of the aggregates, light scattering turbidity measurements could be performed. This involves measuring the amount of transmitted light, and thereby calculating the light absorbed, by particles in suspension. The amount of light absorbed and so the concentration will depend on the size and number of particles. Aggregation and presence of light-scattering particles complicated data processing for the determination of ion-pairing constants by titration method.

2.2.3 Effect of temperature on ion-pairing: Melting method

The failure to determine association constants for 1•2 from the titration experiments due to light-scattering turbidimetric effects led to an attempt to perturb the ion-pairing equilibrium by temperature. If it were possible to completely break the complex by heating the solution containing the salt or if we could study the formation of the complex from the constituent ions we could get thermodynamic information about the ion-pairing. It would be then possible to determine free energy of the system in terms of ΔH, ΔS and ΔG of ion-pairing. These would be direct outcome of the relationship between K_d versus 1/T, where K_d is the equilibrium constant for the dissociation of ion-
pair. We would then be able to determine the association constant, $K_{ip}$, of the ion-pairing as $K_{ip}$ is $1/K_d$.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

At equilibrium,

$$\Delta G^0 = -RT\ln K_{ip}$$

2.2.3.1 Results and Discussion

![Graphs showing the effect of temperature on ion-pairing](image)

**Figure 2.6** Effect of temperature on ion-pairing (a) 1(O)$_3$•2(O)$_3$; (b) 1(O)$_2$(NMe)•2(O)$_3$; (c) 1(O)(NMe)$_2$•2(O)$_3$ and (d) 1(NMe)$_3$•2(O)$_3$

When solutions of 1•2 were heated and the absorbance spectra were recorded at various temperatures during the heating process, it was observed that the long-wavelength absorption due to the complex decreased as the temperature was raised (Figure 2.6). As the temperature increases, the energy, in the form of heat given to the
system, overcomes the intermolecular forces of attraction that holds the ion-pairs together. The contact ion-pairs are intervened by solvent molecules and the ions become solvated separately. When the temperature is sufficiently high such that it can overcome the binding energy, the contact ions-pairs are separated and form loose ion-pairs. With this the long-wavelength absorbance decreases and eventually becomes zero when all the ions-pairs are broken and separated by solvent. The UV-Vis absorption for free cations (non-encumbered) and anion are provided for reference (Figure 2.7).

Figure 2.7 UV-Vis absorption profiles of the four non-encumbered cations and anion at a concentration of 5E-5 M.

2.2.3.2 Experimental

All solutions were prepared in PC. The absorption spectra were acquired by Agilent’s 8453 UV-Vis spectrophotometer attached with peltier temperature controller accessory. The spectra were processed using ChemStation software. The salt pairs 1•2 were dissolved in PC and subjected to sonication in a bath sonicator at 25 °C. The samples were heated to the required temperature and were held at that temperature for a time period, as required by the study, before recording the spectra.

2.2.4 Investigating the long-wavelength phenomenon

Is the long-wavelength absorption due to a 1:1 ion-pair, 1•2? If that had been the case, then it would have been easier to determine $K_{ip}$ by both titration and melting methods. But, as mentioned earlier and as will be discussed later, the determination of $K_{ip}$
was limited by formation of complex ion-pairs of higher order aggregation (e.g., $1\cdot 2\cdot 1$, $2\cdot 1\cdot 2$ or oligomeric). In order to determine if it were a 1:1, 1:2 or 2:1 stoichiometry of the complex that was responsible for the long-wavelength absorption, solutions containing required concentrations of 1 and 2 were mixed in required proportions. All samples were subjected to sonication for 20 min before acquiring spectra.

Figure 2.8 UV-Vis spectra for various ratios of cation and anion (a) 1(O)$_3$ and 2(O)$_3$; (b) 1(O)$_2$(NMe) and 2(O)$_3$; (c) 1(O)(NMe)$_2$ and 2(O)$_3$ and (d) 1(NMe)$_3$ and 2(O)$_3$.

If there were multiple complexes formed, for example, $1\cdot 2$, $1\cdot 2\cdot 1$ or $2\cdot 1\cdot 2$, then the wavelengths for the absorption of these complexes should be different. Since both 1 and 2 are chromophoric, addition of either of them to the contact ion-pair $1\cdot 2$ should shift the wavelength of absorption. The UV-Vis measurements (Figure 2.8), however, did not reveal any major changes in the absorption patterns for the three stoichiometries studied. All the three stoichiometries showed characteristic broad long-wavelength absorption as
was noticed in the previous studies. The solutions containing excess 1 and 2, showed increased absorptions at respective wavelengths of native ions.

Since the determination of the association constants from the melting of the complex did not give a solution to the problem at hand, the possibility of determining $K_{ip}$ by studying the kinetics of complex formation by evolution of the long-wavelength band was explored. This would have been difficult to study by monitoring the formation of complex by mixing solutions with equimolar concentrations of 1 and 2 as this mixing produced salt pair almost instantaneously as a precipitate. Also, the precipitation was quicker with salts having non-encumbered cations. Note that this observation implies formation of new molecular entities upon mixing of solutions of 1 and 2. So, an alternate approach was followed. In this approach, a solution of the required salt pair 1•2 was made in PC. The sample was sonicated for 20 min before measuring the absorbance. The absorbance spectrum of the sample was acquired. The sample was then heated to 90 °C to break the complex and was left to cool to room temperature. The loose ions were left to interact in solution and the complex formation was monitored by observing evolution of long- wavelength absorbance band in the spectra (Figure 2.9).

![Figure 2.9 Evolution of long-wavelength band with time in complexes of (a) 1(O)$_3$ and 2(O)$_3$; (b) 1(O)(NMe)$_2$ and 2(O)$_3$ and (c) 1(NMe)$_3$ and 2(O)$_3$](image)

As noted before, when saturated solutions of 1 and 2 are mixed at room temperature usually an immediate complexation occurs. In general, the solubility of the aromatic salt decreases as the sterics at the edges of the discotic triangulene cation decreases. The complexes thus formed have lower solubility than the individual parent species, thus resulting in precipitation - a kinetic product of the complexation. The rate of ion-pair formation by this method of salt preparation was faster than when the ions were
allowed to mix after melting the complex. The solutions with different stoichiometries of 1 and 2 in this experiment showed very slow evolution of long-wavelength band (Figure 2.9). Also the increase in long-wavelength band absorbance occurred only for a short time as the other competing process of aggregation, removed mass from the solution due to precipitation of the aggregated species. The study was again intercepted by aggregation that caused precipitation of complex. The slow evolution of the complex and the aggregation should be occurring due to formation of oligomers. So the observed absorbance is not the true absorbance of a homogeneous solution.

### 2.2.5 Hypochromism and stacking

The phenomenon of hypochromism has been extensively used as evidence to stacking in various $\pi$-stacked structures found in nucleic acids, proteins, microcrystals, polymers, dyes etc.\textsuperscript{222-229} Hypochromism is characterized by significant decrease in the intensity of the absorption at the wavelength of interest due to strong molecular interactions. In DNA double helix, consisting of stacked nucleic acid bases at interplanar distance of about 3.4 Å, this decrease could be up to 40% less than the mixture of constituent monomers.\textsuperscript{230} The actual value depends upon the base sequence. Many theoretical studies on hypochromism consider the property in the context of changes in complex refractive index,\textsuperscript{225,231,232} light scattering,\textsuperscript{233,234} absorption\textsuperscript{228} etc. Another model considers hypochromism to be a result of a weak dipole-dipole interaction with the light wave.\textsuperscript{223}

When the aromatic chromophores are closely aggregated, their electronic states are perturbed due to interactions. This should affect the absorption spectra of the stack. Hypochromism should arise from face-to-face stacking geometry depending on the distance and orientation between the two aromatic ring planes.\textsuperscript{235} The resulting dipoles should be mutually repelling and so the small transition dipole results in decreased absorption. Upon careful analysis of the absorption of the salts 1•2 of the unencumbered cations, hypochromism is observed upon complex formation, at the $\lambda_{\text{max}}$ of the cation and the anion (Figure 2.2). This observation is a direct indication of face-centered stacking of the aromatic anion and cation where there is no facial encumbrance. Such hypochromism
is not observed when stacking of the discotic faces is blocked due to the angularity in cations with side chain ethyl substitution (Figure 2.3).

The opposite phenomenon, hyperchromism, is observed when the stacking association is affected by heating. So, when the salt 1•2 melts, the intensity around the absorption of 1 and 2 increases (Figure 2.6). The unstacking of the aromatic discotics results in the loss of long-wavelength absorbance.

2.3 Experimental evidences for the presence of complex ion-pairs

A detailed account on attempted determination of association constant by titration and melting experiments will be presented in Chapter 4. The failures of the titration and melting methods in the determination of ion-pairing constant, was mainly due to the presence of complex solution state aggregated ion-pairs that extend into the kinetic regime. The observations from crystalline state and solution state studies gave indications for the presence of oigomeric and polymeric species due to ion-pairing. The polymer that we refer to here is not in reference to the conventional polymer formed by covalent interactions. These are actually ions held together by non-covalent interactions where the interaction between 1 and 2 is more than a simple heterodimeric association of type 1•2.

There are at least a few compelling reasons that lead us to this conclusion. The description to follow will list indicators from various studies that lead us to this logical conclusion.

A former member of Cammers group reported the crystalline state of a variety of cations and salt pairs of type 1•2. Single crystals of salt pairs where the cation has peripheral alkyl and phenyl substitution were studied and the effects of substitution were investigated. In general, the motif changed from a dimer in the solid state of cation to a polymer in the case of salt pair. The salt pair has an alternate arrangement of cation and anion (Figure 2.10 (b)). The cations form a face-to-face dimeric arrangement, with the substituents being placed on the opposite sides of the plane where the aromatic faces interact (Figure 2.10 (a)). The salt pairs have cation and anion associated with the substituents on cation being pushed away from the plane where oppositely charged discs interact. The chain length of the substituent determined how close the aromatic discotics
could approach in the solid state. It was concluded that the angularity of the -CH$_2$- in the alkyl substituents hindered the close approach of anion at both the faces of the cation and the result is a polymer of heterodimer. This picture should be much different with crystalline state of salt pairs with non-encumbered cations. With least sterics at the edges, there should be no hindrance for the approach of anion at both the faces of the cation. So as the chain length of substitution approached zero, the aromatic disotics should be placed at almost the same distance. This could, however, not be studied with single crystal X-ray diffraction due to lack of diffraction quality single crystals.

![Figure 2.10 Solid state motifs of (a) 1(NOct)$_3$ and (b) 1(NOct)$_3$•2.](image)

Curiously, as mentioned above, the solution state absorption measurements again placed the non-encumbered salt pairs in a different group, that had long-wavelength absorbance, showing long-wavelength absorbance, from the salt pairs where the cations had at least one ethyl substituent. The ethyl substituent completely inhibited the formation of long-wavelength absorbing species although a dimer can readily form as evidenced by single crystal studies. The investigation of long-wavelength absorbance in solutions with varying stoichiometry of 1 and 2 (1:1, 1:2 and 2:1) had the long-wavelength absorbance at the same wavelength. All the non-encumbered salt pairs produced nanometric species that scatter light. These observations imply presence of species other than heterodimeric 1•2 in the solution state.

Some evidence of complex ion-pair formation was obtained in the ESI-MS analysis of the salt pairs. The coupled strengths of being a soft ionization technique and
the ability to produce multiply charged ions gives advantage to ESI-MS over other ionization techniques to be used in the study of non-covalent interactions.\textsuperscript{236-247}

This technique has been used to study interactions in the gas phase that could be extended to solution state. The interactions between 1\cdot2 revealed important information on the nature of aggregation in triangulene salt pairs.\textsuperscript{99} Stark contrast in nature of interaction of anion, 2(O)\textsubscript{3}, with trioxa cation, 1(O)\textsubscript{3}, and various triaza cations were found by ionization in both positive and negative modes. While the trioxa cation showed peaks for both 1\cdot2\cdot1 and 2\cdot1\cdot2 relative to 1 and 2 in positive and negative modes respectively, the triaza cations showed preferentially peaks for 1\cdot2\cdot1 relative to 1 in the positive mode. Also the relative abundance for 1\cdot2\cdot1 decreased as the length of side chain alkyl substitution increased.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Angular_group.png}
\caption{Angular group affecting trimer formation in 1(NEt)\textsubscript{3}\cdot2.}
\end{figure}

The absorbance spectra of salts with even one ethyl substituent did not show any long-wavelength absorbance bands (Figure 2.3). The spectra in these salts were same as that of the spectra obtained by linear superposition of the individual constituents. The presence of even one angular substituent prevents close approach of two oppositely charged discs at both the termini of the cationic disc. So in these cases formation of complex ions of the type 1\cdot2\cdot1 and 2\cdot1\cdot2 (Figure 2.11) is very unlikely; and hence no long-wavelength absorbance. Some preference for the formation of 1\cdot2\cdot1 heterotrimer was observed in the ESI-MS analysis of 1(NEt)\textsubscript{3}\cdot2(O)\textsubscript{3}. This small preference can be possibly be explained by comparing the two stacking arrangements, 1\cdot2\cdot1 and 2\cdot1\cdot2. The trimer 2\cdot1\cdot2 is less likely to form because of the blockage of 2(O)\textsubscript{3} from at least from one
face of $1(\text{NEt})_3$ is understandable due to the angularity brought about by three ethyl groups (Figure 2.11 (a)) The other arrangement $1 \cdot 2 \cdot 1$ may not be that energetically challenged as it demands approach of $2(O)_3$ only from one side of $1(\text{NEt})_3$ (Figure 2.11 (b)).

From the data of ESI-MS even the methyl rotor present at the center of the trimeric arrangement, removes the $2 \cdot 1 \cdot 2$ heterotrimer from the trimeric distribution. If we can extend the same preference of distribution to the solution state, then we say that the equilibrium process producing polymeric $1 \cdot 2$ should be much faster in the association of $2(O)_3$ with $1(O)_3$ than with $1(\text{NMe})_3$ because both $1 \cdot 2 \cdot 1$ and $2 \cdot 1 \cdot 2$ are possible in the first case whereas only $1 \cdot 2 \cdot 1$ occurs in the latter.

What is the nature of ion-pairing? What experimental conditions led to the formation of aggregates that muddled quantification of ion-pairing? Can we set up experiments to counter these hindrances? The chapters to follow will attempt to address some of these queries based on what is already known about the nature of aromatic interactions.
Chapter 3
Substitution Dependent Contact Ion Pairing and Solvent-separated Ion Pairs in Solution

3.1 Introduction

In the chemical literature, investigation of ion-pairing in solution phase has been carried out by using various techniques that basically rely on measuring a response due to the formation of a complexed species. Some of the techniques are conductometry (measurement of electrical conductivity), potentiometry, relaxation method (dielectric, ultrasonic, NMR), spectroscopy (electronic (UV-Vis, fluorescence), vibrational (IR, Raman) and magnetic (NMR, EPR)). In this work the solution state behavior of ion-pair 1•2, was investigated by absorption spectroscopy and electrochemistry.

Magnetic resonance techniques, EPR and NMR, are common approaches to measure association constants in solution-state molecular species. Measurement of $^1$H chemical shifts of the associated species can be used to compute association constants. In addition to obtaining quantitative information from an NMR titration, other useful information of relative chemical shifts and effect on symmetry could be inferred from the complexation involving two species that occurs at a rate measurable at the NMR timescale. Such NMR titrations become quite useful if the interacting molecules are non-chromophoric.

An NMR titration could not be employed with triangulene salt pairs, 1•2, due to their very limited solubility in commonly employed NMR solvents like DMSO-d$_6$, CD$_3$CN etc. The distinct absorption features of 1, 2 and 1•2 could have been utilized for the determination of association between 1 and 2 if the system were in equilibrium. So experiments were designed to study how the redox properties of the ions change when they complex (1•2) compared to free 1 and 2.
3.2 Electrochemical Measurements

3.2.1 Background

Cyclic voltammetry (CV) and other related electrochemical methods could be used to study donor-acceptor molecular associations.\textsuperscript{269,270} A redox reaction involves change in the oxidation state of one or more molecules during the process of electron transfer. Information in terms of oxidation and reduction potentials can be gathered from electrochemical measurements. The redox potentials measured are then converted into energy terms to get thermodynamic information of the redox process. The oxidation potential of the donor and the reduction potential of the acceptor measured individually and in the presence of the interacting partner can be used as a measure of the interaction, if any, between the two.

\begin{align*}
\text{Scheme 3.1} & \text{ The oxidation potential of the free anion should be different from when ion-paired. The shift in oxidation potential will determine the extent of interaction.}
\end{align*}

Material chemists often carefully consider control over frontier molecular orbitals (FMO) when designing donor-acceptor based polymeric materials for electronic applications.\textsuperscript{72,73,271-273} Optimal molecular orbital compatibility, in terms of symmetry, is essential for the best possible interaction between two molecules. Measuring ionization potential (IP) and electron affinity (EA) by electrochemical methods is a very common method.\textsuperscript{274-276} These values are then related to molecular orbital energy levels (HOMO and LUMO) respectively by means of Koopman’s theorem.\textsuperscript{277} Koopman’s theorem states that the negative of the eigenvalue of a filled orbital from a Hartee-Fock calculation is equal to the vertical ionization energy of the ion formed due to photoionization. So, the
vertical ionization energies can be directly related to the energies of the molecular orbitals. There are, of course, limitations to Koopman’s theorem.

In a chemical reaction, the most easily available electrons that can be donated are from the HOMO. A higher energy unoccupied level LUMO is the orbital where a molecule can accept electrons. Consider bringing an electron to a molecule from infinity and putting it into the MOs of the molecule. The electron acceptance, or reduction, can be related to EA of the molecule. Experimentally, the energy of the LUMO is negative of the EA of a molecule. Similarly, the electron removal, or oxidation, can be related to the IP of the molecule. Experimentally, the energy of the HOMO is negative of the IP of the molecule.\(^\text{278}\) So, the difference in the energy between HOMO and LUMO (\(\Delta E\)) can be obtained from the difference of IP and EA.

The goal of the study was to determine the effect of ion pairing on the reduction potential of cations and on the oxidation potential of anion. For this, the reduction potential of the free cation, 1, and the oxidation potential of the free anion, 2, was compared with the oxidation and reduction potentials of 1•2. Any interaction between 1 and 2 should be observed in these electrochemical measurements. Since the anion is common to all salt pairs, measuring the oxidation potential of “free” anion versus the ion-pair should give information on the extent of association among various salt pairs. The oxidation potential of the ion-pair should be positively shifted compared to the oxidation potential of the free anion (Scheme 3.1) since ion-pairing should decrease the energy of the HOMO and thereby increasing the oxidation potential.

3.2.2 Cyclic Voltammetry

In a classic CV experiment, a forward followed by a reverse linear potential scan is applied to a working electrode present in the electrochemical cell containing the analyte of interest along with a supporting electrolyte.
Figure 3.1 Schematic cyclic voltammogram for a redox reaction.

If the oxidation of the analyte and the reduction of its oxidized species are accessible, the average of the oxidation peak potential ($E_{pa}$) and the reduction peak potential ($E_{pc}$) can be used to get an approximate formal electrode potential of the analyte redox system by using the equation:

$$E_1 = \frac{E_{pc} + E_{pa}}{2}$$

This formal electrode potential is related to the standard electrode potential, $E^\Theta$, by Nernst equation:

$$E_{1/2} = E^\Theta + \frac{RT}{nF} \ln \left( \frac{\gamma_o}{\gamma_R} \right)$$

where $E_{1/2}$ represents the energy, expressed as potential, at equilibrium, of a redox couple, $E^\Theta$ represents the same electrode potential determined under standard conditions, $R$ is the gas constant, $T$ is the thermodynamic temperature (in K), $n$ is the number of electrons involved in the redox reaction, $F$ is the Faraday constant and $\gamma_o$ and $\gamma_R$ are activity coefficients of oxidant and reductant.
The differences between $E_{1/2}$ and $E^\Theta$ are small and are often ignored. Then the experimental redox potentials are related to the vacuum level by using internal standards like ferrocene/ferrocenium (Fc/Fc\textsuperscript{+}) redox couple.\textsuperscript{279}

The sensitivity of classical voltammetric methods is quite good. However, at lower analyte concentrations (below 1E-5 M), the non-faradaic charging currents caused by the double-layer leads to unacceptably low accuracy of measurement. So, normal pulse and differential pulse, two very popular pulse methods, are used frequently to study redox processes at lower analyte concentrations.

### 3.2.3 Differential Pulse Voltammetry

In DPV the potential is applied in the form of a pulse (Figure 3.2(a)). The currents are measured twice per pulse. The first current measurement is done just before the rise in the potential after the pulse is applied and the second is at the end of the pulse just before it decreases to the baseline. The differential pulse voltammogram is a plot with difference between the two current measurements, called $\Delta I_{\text{pulse}}$, plotted against potential (Figure 3.2(b)). So, the rate of change of current is actually measuring the differential of current. The $\Delta I_{\text{pulse}}$ is significant only when a redox process takes place during current measurement, as then the difference between the non-faradaic components of the two currents is usually insignificant. So, in the absence of a reduction of the analyte at the working electrode, $\Delta I_{\text{pulse}}$ would be zero and the value increases as the potential approaches $E_{1/2}$. The current response is therefore a symmetric peak.

![Figure 3.2](image)

**Figure 3.2** (a) DPV excitation signal; (b) Current measurement from a signal.
3.2.4 Results and Discussion

The electrochemical measurements were made separately for 1 and 2 in the presence of the non-aromatic counter ions. A CV for 2 (Figure 3.3 (a)) was obtained to see if the oxidation potential of 2 was accessible in the potential window of propylene carbonate (PC, #95) (-3.0 to +3.0 V vs Fc/Fc⁺). When ferrocene (Fc/Fc⁺) was used as an internal standard for measuring the oxidation potential of 2, broad peaks were observed that made it difficult to extract the required oxidation potential of 2 from the voltammogram.

DPV being more sensitive due to the fact that the current sampling points allow for the decay of the capacitive current during the experiment, thus producing a more sensitive measurement of the faradic currents, was used to get the electrochemical information. Since it applies a differential to the observed change in current, voltammograms from DPV have sharper peaks that make determination of peak potentials comparatively more accurate than CV. DPV of 2 in supporting electrolyte, with no internal standard (Fc/Fc⁺) added, is shown in Figure 3.3 (b). With Fc as the internal standard, it was observed that the oxidation potentials of Fc and 2 were very close but could be resolved to some extent by DPV (Figure 3.4 (a)). The closely spaced peaks were deconvoluted by employing Gaussian curve-fitting with Origin 7.0 (Figure 3.4 (b)).

![Figure 3.3 CV (a) and DPV (b) of 2 in the supporting electrolyte showing first oxidation potential.](image-url)
In the same way the reduction potentials of various cations were measured. Figure 3.5 depicts a CV of $1(O)_3$ in the supporting electrolyte, specifically showing the first reduction potential measured vs. Fc/Fc$^+$. In general, for the calculations of the redox potentials vs. Fc/Fc$^+$ by CV, $E_{1/2}$ obtained for Fc/Fc$^+$ in voltammograms are set to 0 V (Figure 3.5). Then $E_{1/2}$ for the analyte is obtained and reported vs. Fc/Fc$^+$. Following this method, the first reduction potential of $1(O)_3$ was calculated to be −0.50 V.

Figure 3.4 DPV of $2(O)_3$ with Fc as internal standard (a) and the deconvoluted peaks (b).

Figure 3.5 CV of $1(O)_3$ in the supporting electrolyte showing first reduction potential.
In order to get the information on reduction potentials of the cations by DPV, a negative scan was done. Again, the potential obtained for Fc/Fc\(^+\) is set to 0 V and the reduction potential for the cation is calculated as a shift from Fc/Fc\(^+\). For example, Figure 3.6 (a) is the DPV for \(1(O)_3\) in the presence of Fc/Fc\(^+\). The peak at 0.39 V is due to Fc/Fc\(^+\) and the peak at −0.12 V is due to \(1(O)_3\). To get the reduction potential of \(1(O)_3\), the peak at 0.39 V is set to 0 V (Figure 3.6 (b)) and the resulting shift to peak at −0.12 V is obtained. So, the reduction potential of \(1(O)_3\) is calculated to be −0.51 V vs Fc/Fc\(^+\) by DPV.

![Figure 3.6 Experimental (a) and referenced (b) voltammogram of 1(O)_3 with Fc as internal standard.](image)

The potentials obtained for \(1(O)_3\) by the two methods, CV and DPV, were found to be similar, about -0.50 V. The measurement and extraction of redox potentials vs. Fc/Fc\(^+\) became more difficult with other cations as the reduction potentials shifted to more negative values. This was because of the interference of the broad peak arising from the electrochemical reduction of residual oxygen present in the electrolyte. With this it was difficult to get accurate peak potentials from the CV measurements. Also the irreversible redox behavior of \(1, 2\) and \(1\bullet2\), impeded measurement of meaningful CV. Hence DPV was used as the preferred method for obtaining redox potentials in this study.

### 3.2.4.1 Comparison of reduction potentials of non-encumbered cations

The reduction potentials of the non-encumbered cations decreased with increasing aza substitution (Figure 3.7). \(1(O)_3\), with three oxygen atoms, is more easily reduced
while \(1(\text{NMe})_3\), with three nitrogen atoms, has a comparatively lower reduction potential and is more difficult to be reduced. This observation is in agreement with the observation that the stability of the triangulenium cation increases with the number of aza bridges.\(^{284,285}\) It has been reported\(^{156,157}\) that the trioxa derivative, \(1(\text{O})_3\), is a good electron acceptor and the triaza derivative, \(1(\text{NMe})_3\), is a better electron donor.

![Graph showing comparison of first reduction potentials](image)

**Figure 3.7** Comparison of first reduction potentials of the four non-encumbered cations (1•BF\(_4\)).

### 3.2.4.2 Effect of peripheral substitution of reduction potential of cation

A comparison of the reduction potentials of the triaza cationic derivatives \(1(\text{NMe})_3\), \(1(\text{NEt})_3\) and \(1(\text{NBu})_3\) (Figure 3.8 (a)) showed that the alkyl group substitution did not have much effect on the reduction potential of the cation. The observation is similar to some of the earlier work involving determination of reduction potentials of triangulene cations.\(^{157}\) This can be explained based on the EA of the cations or the ability to put electrons into the LUMO of the cation during the reduction process. The three triaza cations should have similar magnitudes of \(\pi\)-orbital densities of the FMOs as the electron donating alkyl donating groups do not have much effect on the \(\pi\)-system. So, the ability to accept electrons into these energetically similar empty MOs is less likely to be different. The CV studies of the cations indicated that the redox process was not reversible. It was also noticed that the peaks at first reduction potential, in the case of
triaza cations, were relatively broad. The broadness of the peaks with overpotential are indicative of increasingly irreversible systems. The absorbance spectra of salts with even one ethyl substituent did not show any long-wavelength absorbance bands (Figure 2.4). The spectra in these salts were same as that of the spectra obtained by linear superposition of the individual constituents. The presence of even one angular substituent prevents close approach of two oppositely charged discs at both the termini of the cationic disc. So in these cases formation of complex ions of the type $1 \cdot 2 \cdot 1$ and $2 \cdot 1 \cdot 2$ is very unlikely and hence no long-wavelength absorbance (Figure 2.3). Some preference for the formation of $1 \cdot 2 \cdot 1$ heterotrimer was observed in the ESI-MS analysis of $1(\text{NEt})_3 \cdot 2(\text{O})_3$. This small preference can be possibly be explained by comparing the two stacking arrangements, $1 \cdot 2 \cdot 1$ and $2 \cdot 1 \cdot 2$. The trimer $2 \cdot 1 \cdot 2$ is less likely to form because of the blockage of $2(\text{O})_3$ from at least from one face of $1(\text{NEt})_3$ is understandable due to the angularity brought about by three ethyl groups (Figure 2.11 (a))The other arrangement $1 \cdot 2 \cdot 1$ may not be that energetically challenged as it demands approach of $2(\text{O})_3$ only from one side of $1(\text{NEt})_3$ (Figure 2.11 (b)).

\[ \begin{align*}
1(\text{ME})_3 & \quad 1(\text{NEt})_3 & \quad 1(\text{But})_3 & \quad 1(\text{Oct})_3
\end{align*} \]

\[ \begin{align*}
1(\text{O})_3(\text{ME}) & \quad 1(\text{O})_3(\text{NEt}) & \quad 1(\text{O})_3(\text{But}) & \quad 1(\text{O})_3(\text{Oct})
\end{align*} \]

\[ \begin{align*}
1(\text{O})_2(\text{ME})_2 & \quad 1(\text{O})_2(\text{NEt})_2 & \quad 1(\text{O})_2(\text{But})_2 & \quad 1(\text{O})_2(\text{Oct})_2
\end{align*} \]

\[ \begin{align*}
1(\text{O})_3(\text{ME})(\text{NEt}) & \quad 1(\text{O})_3(\text{But})(\text{NEt}) & \quad 1(\text{O})_3(\text{Oct})(\text{NEt})
\end{align*} \]

**Figure 3.8** Effect of alkyl group substitution on reduction potential in mono-, di- and tri-alkyl cations.
On similar lines, comparison of reduction potential in dioxaaza cations, \(1(O)\_2\)(NMe) and \(1(O)\_2\)(NET) (Figure 3.8 (b)) showed that switching from methyl to ethyl substitution does not have much affect on the reduction potential of the cation. Such a pattern is also observed in different oxadiaza cations \(1(O)(NMe)\_2\), \(1(O)(NET)\_2\) and \(1(O)(NMe)(NET)\) (Figure 3.8 (c)) where the substitution of methyl and ethyl do not have any affect on the reduction potential of the cation. Table 3.1 lists the first reduction potential of various cations under study.

**Table 3.1 List of first reduction potential of various triangulene cations under study.**

<table>
<thead>
<tr>
<th>Cation (with BF(_4)(−) as counter ion)</th>
<th>Reduction potential(^a) vs. Fe/Fe(^+) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1(O)_3)</td>
<td>-0.51±0.0008</td>
</tr>
<tr>
<td>(1(O)_2)(NMe)</td>
<td>-0.95±0.0000</td>
</tr>
<tr>
<td>(1(O)(NMe)_2)</td>
<td>-1.33±0.0099</td>
</tr>
<tr>
<td>(1(NMe)_3)</td>
<td>-1.61±0.0042</td>
</tr>
<tr>
<td>(1(O)_2)(NET)</td>
<td>-0.97±0.0071</td>
</tr>
<tr>
<td>(1(O)(NET)_2)</td>
<td>-1.36±0.0048</td>
</tr>
<tr>
<td>(1(NET)_3)</td>
<td>-1.62±0.0141</td>
</tr>
<tr>
<td>(1(O)(NMe)(NET))</td>
<td>-1.35±0.0017</td>
</tr>
<tr>
<td>(1(NBu)_3)</td>
<td>-1.60±0.0156</td>
</tr>
</tbody>
</table>

\(^a\) Reduction potential calculated as average of multiple runs with standard deviation

**3.2.4.3 Ion-pairing effects on electrochemical measurements**

The magnitude of shift in the oxidation potential, compared to free anion, due to ion-pairing should indicate the extent of interaction between the cation and anion. Strong ion-pairing should cause a greater shift in the oxidation potential. This will happen because upon ion-pairing, a fraction of the electrons from the anion will be involved in
interaction by formation of hypothetical bond with the cation. This will change the
electron densities in the cation and the anion. Now with a new resultant electron density,
the potential required to reduce the cation or oxidize the anion would be different after
ion-pairing than when they were not complexed. The magnitude of the shift due to
complexation can give an idea about the formation constant of the complex. This
magnitude of shift ($\Delta E_{1/2}$) can be seen as:

$$\Delta E_{1/2} = E_{1/2(\text{ion-pair})} - E_{1/2(\text{free})} = \frac{-0.059}{n} \left( \ln K_{ip} - m \ln[A] \right)$$

where $E_{1/2(\text{ion-pair})}$ and $E_{1/2(\text{free})}$ are electrode potentials of 1 or 2 in ion-pair and free state
respectively, $K_{ip}$ is the ion-pair formation constant, $m$ is the stoichiometry of the
complexation and $[A]$ is concentration of 1 or 2.

With the information of the reduction potential of the various cations and from the
observations previously made from crystalline state and UV-Vis experiments, there
should be some differences in the potentials upon ion-pairing. The pairing interaction
should produce species in which the oppositely charged ions would be in close proximity
to each other. The resultant species like $1\cdot2$, $2\cdot1\cdot2$, $1\cdot2\cdot1$ etc should have redox
potentials different than the constituent 1 or 2. This is because the electrostatic
interactions between oppositely charged aromatic ions are greater than the interaction
between aromatic ion and a non-aromatic counter.

The shifts in oxidation potential of the ion-pair with respect to the free anion
$2(O)_{3}$ could not be accurately determined due to the complexation of $2(O)_{3}$ with Fc (and
other derivatives of Fc attempted to be used as internal standard). This complexation
produced broad peaks near the expected oxidation potentials and other peaks due to the
resultant species. So to determine the oxidation potential of the salt pairs, Fc in
supporting electrolyte was used as an external standard (see description in section
3.2.4.4). It must be noted that since the redox potentials in ion-pairs were obtained using
an external reference standard, these are only estimated shifts. Accurate measurements
that would rely on using internal reference standard are being planned.
Comparison of the oxidation potential of 2(O)₃ with the oxidation potentials of the salt pairs (Table 3.2) gave some insights into the stability gained by the anion upon ion-pairing. The oxidation potential of 2(O)₃ was determined to be -91±1.3 mV (vs Fc/Fc⁺). Upon ion-pairing with the cations, the oxidation potentials were shifted to more positive values (Table 3.2). This means that the 2(O)₃ is more stabilized in the presence of aromatic cations than in the presence of non-aromatic NBu₄(+) counter as it was more difficult to oxidize. The extent of stability was also observed to be maximum in the presence of 1(O)₃ with a shift of 109 mV in oxidation potential. This is in agreement with previous observations that 1(O)₃ is most Lewis acidic and also has the ability to have best possible MO contact with 2(O)₃.

Table 3.2 List of oxidation potential of various salts under study and the shift in oxidation potential upon ion-pairing.

<table>
<thead>
<tr>
<th>Salt pair</th>
<th>Oxidation potential vs. Fc/Fc⁺ (mV)</th>
<th>Shift in Oxidation potential upon ion-pairing vs. Fc/Fc⁺ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2(O)₃•NBu₄</td>
<td>-91</td>
<td></td>
</tr>
<tr>
<td>1(O)₃•2(O)₃</td>
<td>19</td>
<td>109</td>
</tr>
<tr>
<td>1(O)₂(NMe)•2(O)₃</td>
<td>-53</td>
<td>37</td>
</tr>
<tr>
<td>1(O)(NMe)₂•2(O)₃</td>
<td>-19</td>
<td>71</td>
</tr>
<tr>
<td>1(NMe)₃•2(O)₃</td>
<td>-8</td>
<td>82</td>
</tr>
<tr>
<td>1(O)₂(NEt)•2(O)₃</td>
<td>-68</td>
<td>22</td>
</tr>
<tr>
<td>1(O)(NEt)₂•2(O)₃</td>
<td>-47</td>
<td>43</td>
</tr>
<tr>
<td>1(NEt)₃•2(O)₃</td>
<td>-29</td>
<td>61</td>
</tr>
<tr>
<td>1(O)(NMe)(NEt)•2(O)₃</td>
<td>-42</td>
<td>48</td>
</tr>
<tr>
<td>1(NBu)₃•2(O)₃</td>
<td>-41</td>
<td>49</td>
</tr>
</tbody>
</table>
Increasing the aza substitution on the cation also had some effect on the oxidation potentials of the salt pairs. Comparing the shifts in oxidation potential of $2(\text{O})_3$ upon ion-pairing, among the four non-encumbered salt pairs (Figure 3.9 (a)), it was observed that the symmetrical cations, $1(\text{O})_3$ and $1(\text{NMe})_3$, showed greater shifts in the oxidation potential upon ion-pairing than the symmetry-breaking cations, $1(\text{O})_2(\text{NMe})$ and $1(\text{O})(\text{NMe})_2$. So the symmetrical cations seem to have better interaction with anion than the dissymmetrical cations thus increasing the oxidation potential in their presence. This would be expected since the face-to-face contact should be quite enhanced upon interaction with symmetrical cations. This can be understood in terms of the electrostatic potential of the cation. The cations, $1(\text{O})_3$ and $1(\text{NMe})_3$, should have a symmetrical distribution of the positive potential on the surface. The symmetrical anion, $2(\text{O})_3$, with complimentary symmetrical negative potential will have a better interaction with symmetrical distribution of opposite potential (in $1(\text{O})_3$ and $1(\text{NMe})_3$). The interaction with dissymmetrical positive potential distribution in cations $1(\text{O})_2(\text{NMe})$ and $1(\text{O})(\text{NMe})_2$ will likely be comparatively less stronger. So, in this case the possibility of oxidation of anion is slightly increased which is reflected by a decreasing shift in oxidation potential (Table 3.2).

![Figure 3.9](image.png)

**Figure 3.9** Comparing shifts in oxidation due to ion-pairing in the series of salt with (a) increasing the number of methyl substituents and (b) increasing the number of angular substituents.
Comparing the effect of increasing angular substituents among the salts containing the cations \(1\text{(O)}_2\text{(NEt)}\), \(1\text{(O)}(\text{NEt})_2\) and \(1\text{(NEt)}_3\) (Figure 3.9 (b)), it was observed that the shifts in oxidation potential was less than the shifts in non-encumbered salts. This is because the angular group blocks the close approach. The effects here seem to be due to combined effects of symmetry and angularity.

The steric effects due to angular substituents was also noticed to some extent in the ion-pairing of \(2\text{(O)}_3\) with \(1\text{(NMe)}_3\), \(1\text{(NEt)}_3\) and \(1\text{(NBu)}_3\). The sterically unencumbered cation \(1\text{(O)}_3\) stabilized \(2\text{(O)}_3\) to a maximum extent due to good a facial contact. Curiously a difference due to the methyl rotor in \(1\text{(NMe)}_3\) could also be observed by comparing the shifts in oxidation potentials among the respective salts. The facial contact is blocked by the angular substituents in \(1\text{(NEt)}_3\) and \(1\text{(NBu)}_3\). Increasing the alkyl chain length decreases the intimacy with \(2\text{(O)}_3\). So the shift in oxidation potential of \(2\text{(O)}_3\) upon ion-pairing with triaza cations decreases with increasing alkyl chain length as the oxidation becomes comparatively easier (Figure 3.10).

![Figure 3.10 Comparing shifts in oxidation due to ion-pairing in the series of salts with increasing the length of the alkyl side chain on the cation.](image)

3.2.4.4 Experimental

Voltammetric measurements, CV and DPV, were performed using a CH Instruments 650E potentiostat. The electrochemical measurements were performed using
a conventional three-electrode system with a 3 mm diameter glassy carbon as the working electrode, platinum wire as the counter electrode, and freshly anodized silver/silver chloride as the reference electrode. Voltammograms were recorded at scan rates of 100 mV s\(^{-1}\) (CV) or 10 mV increments in DPV. The electrolyte consisted of 0.1 M \(n\text{Bu}_4\text{NPF}_6\) in PC and contained 5E-4 M of analyte 1 or 2 when recorded individually and 2.5E-4 M when mixed to form the complex 1•2. Ferrocene was added to each sample as an internal reference. But since it was observed that the peaks for 2(O)\(_3\) were very close to Fc and it was difficult to deconvolute them, it was decided to use the data with Fc as external reference for the calculation of redox potential. In order to do this, typically the shift of residual oxygen was obtained with Fc as internal standard in the case of cations. This shift for residual oxygen was set to the exact potential in the case of ion-pairs. The redox potentials for the ion-pairs were then calculated accordingly. Multiple runs were performed for each sample to assure reproducibility. All measurements were made at room temperature. The values of redox potentials obtained were within ±0.015 V in multiple attempts.

### 3.2.4.5 Conclusions

A comprehensive electrochemical analysis of the salt pairs was restricted due to solubility limitations of 1•2 in PC. The oxidation potentials of 2(O)\(_3\) and Fc/Fc\(^+\) were also close such that resolution of oxidation peaks was difficult. It was also observed that Fc/Fc\(^+\) was interacting with 2(O)\(_3\) and produced currents due to the redox properties of the complex formed. Further complications in the system are also expected. The cations and the anion are both aromatic. The products of the reduction or oxidation of the aromatic ions would produce aromatic radicals that could interact with the cations or anion present in the solution.

Even with these potential complications, important conclusions could be made in terms of redox properties of ion-pairs with non-encumbered cations that showed decreased intensity of electrode currents at the oxidation and reduction potentials upon mixing when compared to the uncomplexed ions. It was observed that the reduction potential of 1 did not change upon ion-pairing. However, considerable changes in the oxidation potential were observed with 2(O)\(_3\) upon ion-pairing. The shifts were affected
by symmetry and the nature of alkyl substituent on the cation involved in ion-pairing. Increasing the number of nitrogen atoms on the cation, resulted in the decrease in the reduction potential due to greater stability bestowed by the aza substituent (Table 3.1). Increasing the alkyl chain length in related mono-, di- and tri-aza substituted cations did not cause much effect on the reduction potential (Table 3.1). The oxidation potential of the ion-pair was dependent on the effects produced by the symmetry and the length of the alkyl substituent on the cation involved in ion-pairing. The related mixed aza-oxa combination, the symmetrical cations showed greater effect on the oxidation potential upon ion-pairing (Table 3.2). Increasing the alkyl substituent length on the triaza cation, decreased its interaction with \(2(O)\) upon ion-pairing and thus caused a shift towards ease of oxidation of \(2(O)\).

### 3.3 UV-Vis Absorption Spectroscopy

#### 3.3.1 Introduction

The following section will describe the attempts to determine ion-pairing constants from the data obtained by two experimental approaches: titration and melting. The only assumption made in this analysis is that the complex formed is a discrete species with a non-zero molar absorptivity. As it has been mentioned before these equilibrium principles could not be applied to the ion-pairing in solution as it turned out to be kinetic phenomenon leading to aggregation and slow precipitation of the material from solution which muddled the determination of any association. The most obvious clue was the slow evolution of the long wavelength phenomenon that appears at various wavelengths (Figure 2.9). In all cases the solutions slowly evolved solids at room temperature. In all cases the evolution of the long-wavelength species was immediate upon mixing the discotics and showed strong hysteresis in variable-temperature UV spectra. Various attempts to reach equilibrium via concentration, temperature, ionic strength etc. did not help in establishing equilibrium. The following approach should be still applicable if a concentration- or a temperature-based equilibrium in solution could be attained.
3.3.2 Attempted determination of equilibrium constant for ion-pairing ($K_{ip}$) by titration

3.3.2.1 Background

A standard binding constant determination experiment involves titration performed by keeping the concentration of one the species (analyte of interest) constant while varying the concentration of the other (titrant). The physical changes in the system accompanied by complexation, usually spectroscopically, are monitored. This change in the property is then plotted as a function of concentration of titrant. A mathematical model (binding isotherm), used to obtain the association constant, is also typically developed based on the physical change or the property being monitored. The model is then correlated to the concentration of complex.

As the triangulene cations and anion have absorptions in the UV-Vis region, either of them could be used as the analyte. Titrations in both ways were attempted, keeping cation constant and varying anion and vice versa, and it was observed that the absorption due to the complex could be followed to study ion pairing. Since the results were found to be converging, to compare the extent of association of various cations with the anion, an easier approach seemed to use the anion, 2, as the analyte and cation, 1, as the titrant. The titration data were analyzed to determine association constant as described below.

3.3.2.2 Mathematical model for binding constant determination

Binding constants determination have typically relied on linear regression by the evaluation of slope and intercepts. Some of the popular methods like Benesi-Hildebrand, Lineweaver-Burk, Scathard plots have inherent problems with many assumptions that violate linear regression and the results could be frequently misleading. A usual requirement of these methods requires one of the species, usually acceptor, to be at a much higher concentration than the other. Such methods are reliable only in limited cases. With the availability of modern nonlinear regression methods backed by the computing powers, the other older methods are quickly disappearing. Nonlinear regression is much more complicated and involved than linear regression and requires an iterative approach.
The following model has been used for determining ion-pairing constant in triangulene salt pairs. Consider the ion-pairing equilibrium,

\[ \mathbf{1} + \mathbf{2} \rightleftharpoons \mathbf{1} \cdot \mathbf{2} \]

Let the absorption of the complex at a given wavelength (\(\lambda, \text{nm}\)) is \(A\). Then we can define \(A\) in terms of the molar absorptivities (\(\varepsilon\)) and concentrations of cation (1), anion (2) and the complex \(1 \cdot 2\).

\[ A = \varepsilon_1[1] + \varepsilon_2[2] + \varepsilon_{12}[1 \cdot 2] \quad (3.1) \]

From an expression for association (ion pairing) constant

\[ K_{ip} = \frac{[1 \cdot 2]}{[1][2]} \]

\[ [1 \cdot 2] = K_{ip}[1][2] \quad (3.2) \]

We can rewrite equation 3.1 in terms of equation 3.2 as

\[ A = \varepsilon_1[1] + \varepsilon_2[2] + \varepsilon_{12}K_{ip}[1][2] \quad (3.3) \]

The total concentration of 1 can be defined as

\[ [1]_0 = [1] + [1 \cdot 2] \quad (3.4) \]

or,

\[ [1]_0 = [1] + K_{ip}[1][2] \quad (3.5) \]

\[ [1] = \frac{[1]_0}{1 + K_{ip}[2]} \quad (3.6) \]

Similarly, we can define total concentration of 2 as

\[ [2]_0 = [2] + [1 \cdot 2] \quad (3.7) \]

or,

\[ [2]_0 = [2] + K_{ip}[1][2] \quad (3.8) \]
[2] = \frac{[2]_0}{1 + K_{ip}[1]} \quad (3.9)

Substituting equation 3.9 into 3.6, we will get

[1] = \frac{[1]_0}{1 + K_{ip}\left(\frac{[2]_0}{1 + K_{ip}[1]}\right)} \quad (3.10)

In the above expression, only [1] is unknowable. This is same as

[1] = \frac{[1]_0}{\frac{[2]_0 K_{ip}}{1 + K_{ip}[1]}} \quad (3.11)

Taking an inverse of equation 3.11 will give,

\frac{1}{[1]} = \frac{1 + \frac{[2]_0 K_{ip}}{1 + K_{ip}[1]}}{[1]_0} \quad (3.12)

Rearranging equation 3.12 will give

[1]_0 = \frac{[1] + [1][2]_0 K_{ip}}{1 + K_{ip}[1]} \quad (3.13)

[1]_0 + K_{ip}[1]_0[1] = [1] + [1][2]_0 K_{ip} \quad (3.14)
Dividing equation 3.14 by $[1]$, we will get

$$\frac{[1]}{[1]} + K_{ip}[1]_0 = 1 + [2]_0K_{ip}$$

(3.15)

After rearranging and further simplifying, we can write an expression for $[1]$ as

$$[1] = \frac{[1]_0}{1 + [2]_0K_{ip} - K_{ip}[1]_0}$$

(3.16)

With $[1]$ known, we can write an expression for $[2]$ simply by substituting equation 3.16 into 3.9

$$[2] = \frac{[2]_0}{1 + \frac{K_{ip}[1]_0}{1 + [2]_0K_{ip} - K_{ip}[1]_0}}$$

(3.17)

Using the expressions for $[1]$ and $[2]$ from equations 3.16 and 3.17, substituting them into equation 3.3 would give us

$$A = \frac{\varepsilon_1[1]_0}{1 + [2]_0K_{ip} - K_{ip}[1]_0} + \frac{\varepsilon_2[2]_0}{1 + \frac{K_{ip}[1]_0}{1 + [2]_0K_{ip} - K_{ip}[1]_0}} + \frac{\varepsilon_{12}K_{ip}[1]_0[2]_0}{(1 + [1]_0K_{ip})}$$

(3.18)

In the regions where $\varepsilon_1 = \varepsilon_2 = 0$, that is in the region where only the complex absorbs, equation 3.18 simplifies to

$$A = \frac{\varepsilon_{12}K_{ip}[1]_0[2]_0}{(1 + [1]_0K_{ip})}$$

(3.19)
And if we divide the absorbance of the complex with the concentration of cation ([1]₀) added to the anion,

\[
\frac{A}{[1]_0} = \frac{\varepsilon_{12}K_{ip}[2]_0}{(1 + [1]_0K_{ip})}
\]

(3.20)

Since the absorbance is directly proportional to concentration, the absorption due to the complex for constant [2]₀ would be directly proportional to the amount of [1]₀ added and can be related as

\[
A_{\text{max}} = \varepsilon_{12}[2]_0
\]

(3.21)

or

\[
\varepsilon_{12} = \frac{A_{\text{max}}}{[2]_0}
\]

Substituting equation 3.21 into 3.19 and rearranging, we will get

\[
\frac{A}{A_{\text{max}}} = \frac{[1]_0K_{ip}}{1 + [1]_0K_{ip}}
\]

(3.22)

Dividing equation 3.22 by \(K_{ip}\), we will get

\[
\frac{A}{A_{\text{max}}} = \frac{[1]_0}{K_d + [1]_0}
\]

(3.23)

where \(K_d\) (dissociation constant) = 1/\(K_{ip}\) (association constant).

Then we can express equation 3.20 in terms of \(K_d\) as

\[
\frac{A}{[2]_0} = \frac{\varepsilon_{12}[1]_0}{(K_d + [1]_0)}
\]

(3.24)
In the above expression (equation 3.24), \([1]_0\) is the concentration of titrant (cation), \([2]_0\) is the concentration of the analyte (anion) and \(A\) is the absorbance due to the complex for each \([1]_0\).

### 3.3.2.3 Non-linear data analysis by MatLab

Once the model is developed to relate change in \(A\) with \([1]_0\), nonlinear regression fits the model to the data. We used MatLab (matrix laboratory) to fit the experimental data with the binding isotherm.

MatLAB developed by MathWorks, is a computing environment to facilitate numerical analysis. The specific utility used in MatLAB was NLFit, a nonlinear regression protocol that allows the user to enter a discrete function with defined parameters to optimize via the least squares technique.

\[
A(c)\lambda = \text{nlinfit}(X,Y,\text{modelfun},\text{beta0})
\]
returns a vector of estimated coefficients for the nonlinear regression of the responses in Absorbance as a function of concentration as a function of wavelength, \(A(c)\lambda\), using the mathematical model, modelfun, defined by the user. The coefficients defined in modelfun are optimized using iterative least squares protocol, with initial values specified specified by the user in beta0. For a more general description see: [http://www.mathworks.com/help/stats/nlinfit.html](http://www.mathworks.com/help/stats/nlinfit.html).

This model and the method of analysis have been set up by Dr. Arthur Cammers.

### 3.3.2.4 Results and Discussion

Several attempts of crystallizing aromatic salts \(1\cdot2\) (salts with nonencumbered cations) did not yield any X-ray quality crystals. Low solubility and mostly due to their nature of forming aggregates, crystallization of \(1\cdot2\) in many solvents resulted in formation of precipitate or very tiny crystals that were not suitable for x-ray analysis. Due to the unavailability of any single crystal x-ray data it was difficult to know exactly how strongly the unhindered cations and anion interacted in solid state. However, based on the knowledge of the solid-state behavior of the cations \(1\) and from other known \(1\cdot2\), solid state behavior of the unknown salts \(1\cdot2\) could be estimated.
The salts 1•2 containing cations with peripheral alkyl or phenyl substitution showed alternate arrangements of 1 and 2 in a 1D columnar fashion. Typically two out of the three substituents were placed towards one side of the aromatic cationic face and the third substituent was placed on the opposite side. This unsymmetrical arrangement of substituents produced less intimate and more intimate interactions on either side of the cation with the anion in the solid state. So the crystal structures showed alternating short inter-discotic distances and long inter-discotic distances. As a model for solution-state behavior putative dimers might have short distances between the cation and the anion, but the trimer 2•1•2 would be required to have the long and the short inter-discotic distances. The cartoon in Figure 3.11 depicts how the encumbered cation hinders association with the second anion. Hypothetically the 1•2•1 trimer could potentially exist with intimate, symmetric inter-discotic distances.

In essence, non-optimal association of 1 and 2 in the salts pairs was due to the steric encumbrance of the side chain alkyl or phenyl substituents in the stacking plane blocking the two sides of the cation for close approach. With least substitution at the
edges, we can envisage a polymeric arrangement of alternate ions in a 1D columnar fashion.

Indications to the polymeric behavior of aromatic salts in solution state were evidenced in the titration study; although we were slow to recognize them. This was evidenced by immediate formation of species causing long-wavelength absorbance and the slow precipitation of material from the solution. The material producing the spectra in Figure 3.12 is not in equilibrium with the solid state. On the contrary, it was slowly (over hours) evolving colloidal and macroscopic polymers, which turned the mixtures turbid and eventually precipitated.

With strong interactions between molecules, they can form aggregates in solution. Aggregation has strong dependence on concentration. At low concentrations, the equilibrium constant for the formation of aggregates might be sufficiently low to allow for stable translucent solution states, but as concentration increases, the amount of aggregation forms higher molecular weight species in solution. In this case the UV baseline increases in a wavelength independent manner – see spectrum (a) in Figure 3.12 due to chemical species that are on the order of wavelength, $\lambda$ (nm), in size.

In the absorbance spectra from the titration experiments (Figure 3.12), broad absorption peaks were observed in the long-wavelength region of the complexes. Broad absorbance bands, from about 900 nm to 1100 nm, were very prominent in the spectra of $1(O)_3\cdot2(O)_3$. Following Beer-Lambert law, the high absorbance should be a direct measure of the high concentration of the absorbing chromophore in a solution. As the concentration increases, the probability of formation of molecular aggregates also increases. As previously mentioned, when solutions of oppositely charged triangulene ion are mixed, immediate precipitation occurs. With lower steric at the edges of the triangulene cations, the resulting salts $1\cdot2$ were increasingly difficult to retain in solution at a higher concentration for a long time in most of the solvents attempted.
Figure 3.12 MatLab output plot and data fitting for the titration of $2(\text{O})_3$ with non-encumbered cations (a,b) $1(\text{O})_3$; (c,d) $1(\text{O})(\text{NMe})$; (e,f) $1(\text{O})(\text{NMe})_2$ and (g,h) $1(\text{NMe})_3$. 

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Considering the above mentioned observations and the correlation of absorption on spectral broadening, the observed broadening can be explained as non-specific aggregation. So, the peak shape may be a measure of aggregation with broader peaks indicating higher order of aggregation.\textsuperscript{294} As discussed in Chapter 2, attempts to study the time-dependent evolution of long-wavelength absorption was limited due the precipitation of the complex even before possible formation of trimeric or oligomeric species after heterodimerization.

Existence of colloid-size, complex ions was also evidenced by the presence of a notable elevation in the baseline in the spectra of \(1(O)_3\cdot2(O)_3\) from about 700 nm to 1100 nm (Figure 3.12 (a)). The spectral elevation or the baseline elevation is an increase in the optical density at all wavelengths due to light scattering. It was observed that as concentration of titrant 1 increased, the absorption curves tend to retain isosbestic points around 580 nm and 680 nm for \(1(O)_2(NMe)\cdot2(O)_3\), \(1(O)(NMe)_2\cdot2(O)_3\) and \(1(NMe)_2\cdot2(O)_3\) but not so for \(1(O)_3\cdot2(O)_3\). Since the wavelength of the isosbestic point should be independent of the concentration of the species in solution as the concentration-dependent equilibrium takes the mixture from one dominant species to the next, the fact that all the curves don’t cross the same isosbestic point indicates that there are various species in a complex equilibrium. The multiple drifting isosbestic points throughout the titration indicate the formation of multiple molecular complexes. The presence of multiple isosbestic points infers operation of multiple equilibria and the simultaneous presence of more than two absorbing species.\textsuperscript{213,295,296}

Even with the above problems the NLFit protocol was implemented in MatLab to output \(K_{ip}\), but it was later realized that the system was never at equilibrium. So, even though the experimental data ‘fits’ well with the binding isotherm, it cannot be used to estimate \(K_{ip}\). Also, the results were not reproducible as it was difficult to reach the same aggregation state each time.

3.3.2.5 Experimental

All solutions were prepared in PC. Absorption studies were carried out on Agilent’s 8453 UV-Vis spectrophotometer at room temperature and processed using ChemStation software. The stock solutions of required concentrations of 1 and 2 under
study were prepared in a volumetric flask. Since the concentration of 2 needs to be kept constant, same aliquot of anion from the stock solution was transferred into various 5 mL volumetric flasks. Varying amounts of 1 was then introduced into the volumetric flasks containing 2. Usually a color change due to complexation occurred almost instantaneously. All the mixtures were diluted to the same final volume (5 mL) in the volumetric flask with PC. After all the dilutions were made, the samples were sonicated in a bath sonicator kept at 25 °C till the precipitated complex was soluble in the solvent. Bath sonicators typically have a tendency to warm up with increased period of usage. It was observed in some experiments that if the samples were sonicated for long period of time that caused an increase in the temperature of the solutions, bands due to the complex were not observed in the spectra. So it was important to maintain the bath temperature below 25 °C. Care should be taken with higher concentration complexes that need slightly longer sonication periods. Absorption spectra of the samples were usually acquired within about 15 min of sonication. It was observed that the complex precipitated out of the solutions slowly.

3.3.3 Attempted determination of equilibrium constant for ion-pairing ($K_{ip}$) by melting method

The following is a description of the model we planned to use for the analysis of UV-Vis data from melting of the complex to obtain the dissociation constant. If we started with salt pair 1•2 dissolved in a solvent, from what was established before,

$$\frac{A}{A_{\text{max}}} = \frac{[1]_0}{K_d + [1]_0}$$

(3.23)

So,

$$K_d = \frac{[1]_0 A_{\text{max}}}{A - [1]_0}$$

(3.25)
Then,

\[ K_d = [1]_0 \left( \frac{A_{\text{max}}}{A} - 1 \right) \]

(3.26)

\[ \frac{\Delta H_{\text{ip}}}{RT} - \frac{\Delta S_{\text{ip}}}{R} = -\ln K_{\text{ip}} \]

(3.27)

\[ \frac{\Delta H_{\text{ip}}}{T} - \Delta S_{\text{ip}} = R \ln K_d \]

(3.28)

Combing 3.26 and 3.28, we can establish relation between relation between temperature and absorbance to deduce \( \Delta H_{\text{ip}} \) as the slope and \( -\Delta S_{\text{ip}} \) as the intercept.

\[ \frac{\Delta H_{\text{ip}}}{T} - \Delta S_{\text{ip}} = R \ln [1]_0 \left( \frac{A_{\text{max}}}{A} - 1 \right) \]

(3.29)

Figure 3.13 Comparison of the spectra of salt pairs 1•2 before and after melting with the spectra of the constituent ions a) 1(O)\(_3\)•2(O)\(_3\); b) 1(O)(NMe)\(_2\)•2(O)\(_3\); and c) 1(NMe)\(_3\)•2(O)\(_3\).

Again, we could not use these methods to determine ion-pairing constant as the solutions were far from equilibrium although melting the salt completely produced spectra that resembled closely to linear superposed spectra of constituent 1 and 2 (Figure
3.13). Cooling the solution of the melted complex did not produce the ion-pair immediately. The ions appear as solvent-separated (with no interaction) until over a period of time when the ion-pair precipitates out.

3.3.4 Job’s method for stoichiometry

Stoichiometry of association in the salt pairs 1•2 was studied by Job’s method. This involves a continuous variation in mole fractions of the soluble components in a series of solutions keeping the sum of the total (eg. substrate + ligand) mole fraction constant. Any property whose value changes with complex formation is measured and correlated to the stoichiometry of the complex formed. Absorption spectroscopy has been widely used for complexes that show absorption at wavelengths where the interacting molecules do not absorb.

The stoichiometry of ion-pairing 1•2 in the complexes, where 1 is non-encumbered, was explored by following the long-wavelength absorbance band. This method could not be used with complexes where the cations presented facial encumbrance because of the absence of spectral bands other than for 1 and 2.

3.3.4.1 Results and Discussion

The plot of long-wavelength absorbance band versus mole fraction of 2 (Figure 3.14) should be carefully interpreted. The results obtained here can only be used as indicator of different stoichiometry of association as the complexes formed are weak unlike metal-ion complexes. Although the plots show one major complex in solution, with the presence of more than one complex in the solution the Job’s method becomes unreliable. When aggregation occurs in solution, complexes of different stoichiometry coexist in the solution. The complexes formed will have different physical property. In that case the assumption that the value of the property being monitored to change would not vary linearly with concentration. Again in the case where aggregates form, Job’s method is not reliable. The observed deflections in the Job’s plot other than at $A_{\text{max}}$ can only imply presence of other complexes. In the same manner, it would be difficult to differentiate between heterodimeric (1•2) and polymeric -(1•2)$_n$- based on the observation of only one inflection point. Another factor that may be limiting the determination of solution phase stoichiometric information is that these solutions are not
at equilibrium. Any loss of mass from solution due to less soluble aggregate would contribute to error in the determination of stoichiometry.

Figure 3.14 Job’s method for determining stoichiometry in complexes (a) 1(O)₃ and 2(O)₃; (b) 1(O)(NMe)₂ and 2(O)₃ and (c) 1(NMe)₃ and 2(O)₃.

3.3.4.2 Experimental

All solutions were prepared in PC. Absorption studies were carried out on Agilent’s 8453 UV-Vis spectrophotometer at room temperature and processed using ChemStation software. Stock solutions of same concentration and volumes of 1 and 2 were prepared separately. The individual solutions were mixed in different volumes to get different mole fractions of individual ions. The total mole fraction in all the solutions was kept constant. All the solutions were sonicated for 20 min in a bath sonicator maintained at 25 °C before acquiring absorption spectra.

3.4 Ionic Strength and its effect on ion-pairing

As mentioned earlier, the complexes 1•2 without steric encumbrance produced π-stacked aggregates in the solvents used for the study. These were also characterized by formation of nonmetric species that caused turbidity in the samples. These interactions were likely strongly electrostatically driven. The question to answer was if we could find an ionic strength where the interactions between the cation and the anion could be equilibrated. In that case the aggregation due to ion-pairing could be regulated to reach a thermodynamic state. In order to check this, various salts were attempted.

In solution state studies, salts have been used to control ionic strength. For example, both synthetic and biological electrolytes have been used in the study of
protein-protein interactions like crystallization, precipitation and stability. However, it has been extremely challenging to rationalize how the ions of the salts interact with proteins and modulate protein solution behavior. In the case of proteins, this seems to be due to interaction of salts with ionic side-chain that result in unfolding of proteins.

The effect of ionic strength on electrostatic interactions in solutions is well known. Increasing the ionic strength of the medium decreases the effective electrostatic interactions between the ions. This occurs because when salts are added to solutions of ionic complexes, they decrease the formation constant of complex by creating an ionic atmosphere that shields the ion interaction.

3.4.1 Increasing ionic strength of the medium with tetrabutylammonium bromide ($n$-NBu$_4$Br)

![Figure 3.15 Effect of ionic strength ramp with n-NBu$_4$Br on 1(O)$_3$$\cdot$2(O)$_3$ in PC.](image)

To check the effect of increasing ionic strength, 1(O)$_3$$\cdot$2(O)$_3$ was subjected to a medium containing $n$-NBu$_4$Br. In this experiment, to a 1E-4 M solution of 1(O)$_3$$\cdot$2(O)$_3$ in PC was added $n$-NBu$_4$Br in small increments. It was observed that the long-wavelength absorbance band decreased with increasing ionic strength. This was also accompanied by decrease in aggregation that lowered the baseline in the regions 700-900 nm (Figure 3.15).
Another important observation was that the absorbance in the cationic region, around 460 nm, also decreased with increasing ionic strength. So it was very likely that the species causing long-wavelength absorbance was interacting with \( n\)-NBu\(_4\)(+) and Br(−) in a way to dissociate the ion-pair. The “free” ions formed were now available to interact with non-chromophoric counter ions. The interaction between \( 1(O)_3 \) and Br(−) seems to be so strong that the peaks characteristic of \( 1(O)_3 \) were completely missing from the UV-Vis spectra in the solutions at relatively high ionic strength (Figure 3.16). The UV-Vis at this ionic strength seemed to closely resemble presence of “free” \( 2(O)_3 \) (Figure 3.16, blue plot). Based on these observations, it was planned to run a Job’s method to determine if it would be possible to make specific ion-pairs and observe them under these conditions spectroscopically.

![Figure 3.16 Comparing spectra of \( 1(O)_3\cdot2(O)_3 \) in the presence and absence of \( n\)-NBu\(_4\)Br.](image)

### 3.4.2 Determining stoichiometry at high ionic strength using \( n\)-NBu\(_4\)Br

Job’s titration was carried out in solutions in which the ionic strength was set to a concentration at which it was established that \( 1(O)_3\cdot2(O)_3 \) do not form intimate ion-pairs. A series of solutions containing variable mole fractions of \( 1(O)_3\cdotBF_4 \) and \( 2(O)_3\cdotNBu_4 \) were mixed keeping the total mole fraction constant. The individual stock solutions of \( 1(O)_3\cdotBF_4 \) and \( 2(O)_3\cdotNBu_4 \) were prepared in PC containing 0.1 M \( n\)-NBu\(_4\)Br. From the
UV-Vis data, there was no observable interaction between 1(O)₃ and 2(O)₃ and only the presence of free 2(O)₃ was detectable which increased with increasing mole fraction of 2(O)₃ (Figure 3.17). Again in this case the identity of 1(O)₃ was masked in the presence of Br(−) and there was no observable interaction between 1(O)₃ and 2(O)₃.

![Absorbance plot](image)

**Figure 3.17** Job’s method in PC containing n-NBu₄Br.

![Scheme](image)

**Scheme 3.2** Specific interaction between 1(O)₃ and Br(−) that quenches the absorbance ~470 nm.

In the two experiments containing n-NBu₄Br, the absorbance due to 1(O)₃ was quenched in the presence of Br(−). This is likely due to specific interaction between highly electrophilic 1(O)₃ and nucleophilic halide Br (−) (Scheme 3.2). In the next attempted experiments, halide ions were replaced by non-nucleophilic anion BF₄(−).

### 3.4.3 Increasing the ionic strength of the medium with n-NBu₄BF₄

Since the dissociation of the ion-pair formed by the association of 1(O)₃ and 2(O)₃ did not work by increasing the ionic strength, a familiar inert salt, n-NBu₄BF₄, was chosen to increase the ionic strength of the medium. Although complete separation of
1(O)₃ and 2(O)₃ was achieved in this medium, as indicated by disappearance of the long-wavelength absorbance band, a high concentration of n-NBu₄BF₄ was required. At high concentration there was scattering resulted in elevation of baseline in the spectra (Figure 3.18).

![Absorbance spectra](image)

**Figure 3.18 Effect of n-NBu₄BF₄ on 1(O)₃•2(O)₃.**

### 3.5 Broad correlations between CV and UV measurements

The UV-Vis transition involves promotion of electrons from the ground electronic state to the excited electronic states. The electrons beings excited by the incident light here are mostly from the outermost occupied molecular orbitals, the HOMO. The energy of the HOMO can be related to the IP of a molecule and the energy of the LUMO to the EA of the molecule. Some information on extent of ion-pairing can be obtained in terms of the energy difference between the HOMO and LUMO of the salt pairs 1•2. There are multiple vibrational states associated with both the ground state and the excited state. The band gap will be the energy difference of the lowest vibrational states of the ground state and the excited states. This difference representing true band gap is difficult to measure as usually broad peaks are observed in the absorption spectrum. Some approximations on this energy gap (optical band gap in this case) can be obtained by considering onset of absorption from the lowest energy absorption of the spectrum. This onset of absorption
can be obtained by extrapolating the spectrum. The wavelength thus obtained can be converted into energy terms by using the Planck equation:

\[ E(f) = \frac{hc}{\lambda(m)} \]

or the energy can be obtained in electronvolts (eV) by:

\[ E(eV) = \frac{1239.84 \text{ eV nm}}{\lambda(nm)} \]

The optical band gaps obtained for the four unencumbered salt pairs are tabulated in Table 3.3.

**Table 3.3 Optical band gaps for unencumbered salt pairs.**

<table>
<thead>
<tr>
<th>Salt pair</th>
<th>Onset of absorption from UV-Vis (nm, #22)</th>
<th>Optical band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(O)₃•2(O)₃</td>
<td>1150</td>
<td>1.08</td>
</tr>
<tr>
<td>1(O)₂(NMe)•2(O)₃</td>
<td>930</td>
<td>1.33</td>
</tr>
<tr>
<td>1(O)(NMe)₂•2(O)₃</td>
<td>840</td>
<td>1.48</td>
</tr>
<tr>
<td>1(NMe)₃•2(O)₃</td>
<td>770</td>
<td>1.61</td>
</tr>
</tbody>
</table>

As was observed with the UV-Vis measurements, the long wavelength absorption band in 1•2 was dependent on the cation identity in the salt pairs where there is no facial encumbrance (Figure 2.3). As the reduction potential of the cation increases, its electron acceptance increases. So, the cation with a higher reduction potential can act as a better acceptor and the energy required for such a transition will be lower.

In the unencumbered salt pairs 1•2, as the ion pairing is being compared among various cations with the same anion, the reduction potential of the salt pair 1•2 should have the same trend as that among the various cations under consideration. The oxidation and reduction potentials can be obtained from the electrochemical measurements. A very broad correlation can be made between the two energy terms measured by optical spectroscopy and electrochemical measurements. Figure 3.19 (a) shows a plot between
$E_{optical}$, which is an estimate of the reduction potential from the optical measurements, versus $E_{red}$, the reduction potential values obtained from the DPV measurements. The two energy terms correlated well with the cation with the highest reduction potential needing lowest energy for the transition of electrons. Accordingly, the complex absorbance band shifted to longer wavelength.

![Figure 3.19 Correlation between UV-Vis and DPV measurements, comparing the UV onset of long-wavelength absorbance with (a) cation reduction potential and (b) calculated electrochemical band gap.](image)

This correlation can be extended to the band gaps measured by optical and voltammetric methods. With the assumption that upon oxidation, the first electron is taken out of the HOMO and upon reduction the electron is put into the LUMO, $E_{ox}$ is a measure of the HOMO and $E_{red}$ is a measure of the LUMO. So, the difference, $E_{ox} - E_{red}$ should be the electrochemical HOMO-LUMO gap that can be obtained in eV. These measurements for the unencumbered salt pairs are presented in Table 3.4.

The electrochemical band gap measurements showed slight variations when compared in similar series of mono-, di- and tri-alkyl substituted derivatives. For example, the difference in the triaza series, it was 1.60 eV for $1$(NMe)$_3$$\cdot$$2$(O)$_3$, 1.58 eV for $1$(NEt)$_3$$\cdot$$2$(O)$_3$ and 1.57 eV for $1$(NBu)$_3$$\cdot$$2$(O)$_3$. This is actually expected because, there was not much change in the reduction potential due to peripheral alkyl substitution.
(Table 3.1) but the oxidation potential changed with greater association in 1(NMe)_3•2(O)_3.

Table 3.4 Electrochemical band gap measurements for non-encumbered salt pairs.

<table>
<thead>
<tr>
<th>Salt pair</th>
<th>Oxidation Potential, E_{ox} (V)</th>
<th>Reduction Potential, E_{red} (V)</th>
<th>Electrochemical band gap, E_{ox}−E_{red} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(O)_3•2(O)_3</td>
<td>0.019</td>
<td>−0.51</td>
<td>0.53</td>
</tr>
<tr>
<td>1(O)_2(NMe)•2(O)_3</td>
<td>−0.053</td>
<td>−0.95</td>
<td>0.90</td>
</tr>
<tr>
<td>1(O)(NMe)_2•2(O)_3</td>
<td>−0.019</td>
<td>−1.35</td>
<td>1.33</td>
</tr>
<tr>
<td>1(NMe)_3•2(O)_3</td>
<td>−0.008</td>
<td>−1.61</td>
<td>1.60</td>
</tr>
</tbody>
</table>

A plot between the band gaps measured by optical (E\text{\textsubscript{optical}}) and electrochemical (E_{ox}−E_{red}) methods (Figure 3.19 (b)) showed the expected correlation among the four non-encumbered salt pairs of interest. The smallest electrochemical band gap obtained was for 1(O)_3•2(O)_3. This was expected from the previous discussion about the highly compatible MO interaction between 1(O)_3 and 2(O)_3 and the highly electrophilic nature of 1(O)_3 making it a much better electron acceptor. So, the electron transition from HOMO of 2(O)_3 to LUMO of 1(O)_3 requires a lower energy, causing the transition to occur at a longer wavelength. The transition shifted to lower wavelengths as the number of nitrogen atoms increased among these four non-encumbered salt pairs. From the reduction potential measurements, 1(NMe)_3 is a better electron donor than an acceptor. So, the long-wavelength signature absorbance bands correlate well with the reduction potential of the cations.

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Chapter 4
Conclusions and Summary

At the beginning of the dissertation, three hypotheses were made:

1) Covalent interaction would be indicated by any dependence of electronic symmetry on ion-pairing energy ($E_{ip}$) (Figure 1.12). If only the electrostatic effect matters the interaction between $2(O)_3$ and all unencumbered derivatives of 1 should be identical to a first approximation.

2) The formation of a covalent bond between Lewis acid and base involves electron transfer. The reduction potential of the Lewis acidic cation is a measure of the electron demand of the cation. Since $2(O)_3$ is the common ion among all the ion-pairs under study, we would expect that in a covalent interaction $E_{ip}$ will depend on the reduction potential of the cation (Figure 1.13). The strength of the interaction should increase with the reduction potential of the cation.

3) A shift in the oxidation potential upon ion-pairing should indicate the extent of interaction. The ion-pairs in which the interaction is stronger will have a higher shift in the oxidation potential compared to the free anion, $2(O)_3$. The plan was to then correlate the extent of these interactions with the thermodynamically derived $E_{ip}$ from UV-Vis measurements. This correlation could not be done because of the limitations in the determination of ion-pairing constants from titration and melting experiments.

The goal of the thesis was to see if the interaction between the two oppositely charged monopoles 1 and 2 is purely electrostatic or has any covalent character to it. Certainly it does not look like the interaction is 100% electrostatic. If this were the case we would not have observed any difference in the electrochemical measurements of “free” ions vs the ion-pairs (Table 3.1). Instead we observed positive shifts in oxidation potential of $2(O)_3$, indicating resistance to oxidation, in the presence of 1 than in the presence of a non-aromatic NBu$_4$(+). The symmetry breaking cations, that is, cations with mixed nitrogen and oxygen substitution, and cations that partially block one or both sides of the $\pi$ face, also caused understandable shifts in oxidation potential (Table 3.2).
The contact between 1 and 2 appears to be chemical. There seems to be some amount of bonding between the two. The interaction between 1 and 2, can be thought in terms of multiele center bonding, as in the case of pancake bonding, which is optimal when the interacting molecules have isosymmetric MOs. This is a direct outcome of the observation that the oxidation potential changed upon ion-pairing. Given that the redox potential measurement should be a measure of the strength of the bond between two species in contact, we observed that increasing the alkyl chain length on the triaza cation decreased its interaction with 2(O)3, making it easier to oxidize upon ion-pairing (Table 3.2). So the bond formed between triaza cation and 2(O)3 gets weaker as the steric effect of the alkyl chain on the face of 1 increases. From MeN to EtN this effect is expected to be quite large, but the effect should fall off with successive additions of -CH2- units.

Any angular substituent on 1 likely inhibited close approach of 2(O)3 and avoided ion-pairs (Figure 3.11) that could possibly be detected by UV-Vis spectroscopy unlike the non-encumbered cations that showed characteristic long-wavelength absorbance phenomenon (Figure 2.2). In contrast, a measureable difference was observed with electrochemical potential measurements as the shift in oxidation potential varied linearly with increasing length of the alkyl substituent on 1 (Table 3.2).

The schematic below (Scheme 4.1) describes the events that occur upon solvent mediated mixing of 1 and 2. The titration and melting experiments were attempted to calculate ion-pairing constant Kip. With this information, thermodynamic details of the system could be obtained. However, these methods could not be utilized due to the hindrance presented by the slow kinetics of aggregation. Solvent mediated mixing of oppositely charged ions, resulted in the formation of suspensions containing nanometric aggregates that caused turbidometric effects leading to elevation in the baseline due to the presence of light-scattering nanometric species. Upon sonication, the aggregates gave way to the formation of sub-nanometric species that are characterized by distinct long-wavelength absorbance band depending on the nature of 1. In all cases, the solutions slowly lead to the formation of precipitate at room temperature upon standing for a few hours.
Scheme 4.1 Events upon solution mediated interaction between 1 and 2.

The objective was to determine the ion-pair association by following this equilibrium (Scheme 4.2):

Scheme 4.2 Expected ion-pairing equilibrium

However, all observations from the attempted experiments lead us to the conclusion that the following is in operation (Scheme 4.2):

Scheme 4.3 Observed ion-pairing reaction
Various attempts of changing solvent, concentration, temperature, sonication time or ionic strength did not help in establishing equilibrium in the system. The experiments aimed at measuring $K_{ip}$ could not be reproduced, as it was difficult to achieve the same solution-state aggregation in each attempt. Since the system is not at equilibrium, $K_{ip}$ is not measurable. These limitations affected determination of association by UV-Vis spectroscopy. However, there were other significant outcomes that came through these studies.

The solution state ion-pairing was strongly steric dependent. Presence of even one angular (ethyl) group as the side chain substituent on the cation blocks the close approach of anion from that side (Figure 3.11). This avoids closely spaced alternate charge-by-charge assembly of the aromatic discs, with the discotic cation having similar inter disc distances to anion on both sides. The interactions in such pairs seem to be ‘frustrated’. On the other hand, the non-encumbered cations have no steric hindrances that would block oligomerization. This was also revealed by formation of particles large enough to scatter light instead of absorb light.

Determination of $E_{ip}$ between various cations and anion could not be quantified from the results of titration and variable temperature UV-Vis experiments. Attempts to put thermodynamic parameters on the $K_{ip}$ were obscured by the presence of complex ions, aggregation and slow kinetics. The extent of aggregation was difficult to quantify but 1(O)$_3$ seemed to aggregate to a larger extent than 1(NMe)$_3$ upon pairing with 2(O)$_3$. This should be likely due to a higher reduction potential of 1(O)$_3$ contributing to the extended interactions.

In this study, it was observed that the long-wavelength band (energy or wavelength) correlated well with the reduction potential of the cation among the four non-encumbered salt pairs (Figure 3.19). Such behavior would be expected because the energy of the cation LUMO should correlate with the reduction potential of the cation and decreasing reduction potential should decrease the energy gap between the anion HOMO and the cation LUMO.
Although the ion-pairing produced species that were capable of scattering light, quantitative light scattering is not feasible with these compounds due to their strong absorbance properties. Since the pairwise interaction absorbed so strongly the turbidity in the solution could not be used to perform quantitative light-scattering studies; these were not attempted.

Future studies

The electrochemical measurements were also affected by complex interactions occurring in the redox system. The interaction of \(2(O)_3\) with ferrocene (and other derivatives attempted) used as internal standard made the determination of shift in oxidation potential due to ion-pairing inaccurate. These could possibly be avoided by using non-aromatic internal standards which would also allow for accurate determination of the shifts upon ion-pairing. In order to quantify %covalency in the face-to-face interaction, diffusion coefficient and molar conductivity studies could be done in addition to obtaining shifts upon ion-pairing.

How would the interaction change with the introduction of sulfur atoms in cations? The electrophilic nature of sulfur atoms should have pronounced effect on the chemical nature of the cation. Sulfur bridged (mono-, di, and tri-) cations could be synthesized. Crystallization of these thiatriangulenes could be attempted with anion. Solution based studies to explore the nature of interactions in these ion-pairs could be performed. The electrochemical nature of the resulting compounds also might be of interest.

A simple \(\pi\)-electron rich donor and \(\pi\)-electron poor acceptor model does not sufficiently form the basis to explain the formation of the complexes observed in this study as we could categorically differentiate the interactions based on sterics of the cation. The interaction seems to be quite dependent on the symmetry of interacting monopoles as it was observed that oxidation potential of the ion-pair was more affected in the presence of symmetrical cations. This is reminiscent of the pancake bonding in \(\pi\)-dimers where efficient overlap of the MOs in symmetry related monopoles is greater (Table 4.3). It was however observed that any angular substituent on the nitrogen atoms of the cation.
hindered the formation of closely placed $\pi$-stacks that had different spectroscopic identity compared to the constituent ions. So, the contact is also distance dependent.

This work was an attempt to answer some fundamental questions related to the nature of aromatic interactions in aromatic $\pi$-stacks. Such interactions find importance in supramolecular assemblies based on biological recognition, materials and, in general, serve as a mode for the construction of new molecules for based on charge-by-charge arrangement. Understanding the conditions that could lead to formation of well-defined $\pi$-stacks should be applicable to the field of materials chemistry, as the donor-acceptor type assemblies possess good electronic properties.
Chapter 5
Synthetic Experimentation

The triangulene cations (1) and anion (2), used in the present study were prepared by following known synthetic methods. The synthesis of cations was largely based on the synthetic methods used by Laursen.\textsuperscript{300,301} The anion synthesis was done by a slight modification of the procedure used by Bushby.\textsuperscript{302}

5.1 Synthesis of cations

Scheme 5.1 Overview of the synthesis of triangulene cations.

Tris(2,6-dimethoxyphenyl) carbenium tetrafluoroborate [3]

In a 3-neck 250 ml RBF fitted with a reflux condenser, was added 1,3-dimethoxybenzene (13.0 mL, 95 mmol) and TMEDA (0.5 mL). To this mixture was added n-BuLi (60 mL, 1.58 M in hexanes) dropwise at room temperature in about 20 min. The light brownish mixture was stirred for another 5 min. A solution of diphenylcarbonate (6.69 g, 31.3
mmol) in benzene (50 mL) was added dropwise in about 10 min into the reaction mixture. The brownish yellow suspension was heated to reflux for 24 h. The reaction mixture was cooled to room temperature and quenched by addition of water. The mixture was diluted with ethyl acetate. The organic layer was separated and washed again with water and brine. Concentration of the volatiles under vacuum yielded light brownish material. This material was dissolved in ethanol (200 mL). Acidification of ethanolic solution with aqueous HBF$_4$ (50% w/w aqueous, 5 mL), followed by addition of diethyl ether (100 mL) and petroleum ether (100 mL) produced dark purple precipitate. The precipitate was collected by filtration and was thoroughly washed with more diethyl ether to produce greenish-black crystals of 3 (12.1 g, 75.89%). $^1$H NMR (400 MHz, CD$_3$CN): $\delta$ 7.62 (t, $J$ = 8.5 Hz, 3H), 6.59 (d, $J$ = 8.5 Hz, 6H), 3.54 (s, 18H). $^{13}$C NMR (100 MHz, CD$_3$CN): $\delta$ 182.7, 163.8, 143.2, 126.5, 106.1, 57.4.

4,8,12-trioxatriangulenium tetrafluoroborate [1(O)$_3$]

To a solution of 3 (1.0 g, 1.96 mmol) in pyridine (10 mL) was added pyridine hydrochloride (10 g). The mixture was slowly heated to 200°C for 3.5 h. The cooled reaction mixture was poured into crushed ice. To this precipitate was added aqueous NaBF$_4$ solution (150 mL, 0.2 M). The aqueous mixture was acidified by addition of HBF$_4$ (50% w/w aqueous). The precipitated material was filtered, washed thoroughly with water, diethyl ether and dried to get the crude product. The crude material was triturated several times with small volumes of dichloromethane (DCM) until the washings were nearly colorless. The material was crystallized from acetonitrile, by slow evaporation of solvent, to yield yellow crystals of 1(O)$_3$ (340 mg, 46%). $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 8.57 (t, $J$ = 8.5 Hz, 3H), 7.98 (d, $J$ = 8.5 Hz, 6H). $^{13}$C NMR (125 MHz, DMSO-d$_6$): $\delta$ 153.0, 145.6, 143.5, 112.6, 105.3.
9-(2,6-Dimethoxyphenyl)-1,8-dimethoxy-10-n-methylacridinium tetrafluoroborate [4(a)]

Methylamine was bubbled for 10 min into NMP (30 mL) cooled in ice. To this solution was added 3 (2.0 g, 3.9 mmol). After stirring the dark red solution at room temperature for 24 h in a sealed tube, the mixture was poured into an aqueous NaBF₄ solution (250 mL, 0.2 M). After acidification with HBF₄ (50% w/w aqueous, 1 mL), the precipitate was collected by filtration and washed thoroughly with water. Recrystallization from methanol gave dark-red crystals of 4(a) (1.6 g; 85.56%). ¹H NMR (400 MHz, CDCl₃): δ 8.18 (t, J = 8.6 Hz, 2H), 8.04 (d, J = 9.2 Hz, 2H), 7.38 (t, J = 8.4 Hz, 1 H), 6.96 (d, J = 8.0 Hz, 2H), 6.66 (d, J = 8.4 Hz, 2H), 4.81 (s, 3H), 3.58 (s, 6H), 3.56 (s, 6H). ¹³C NMR (100 MHz, CD₃CN): δ 161.4, 158.1, 156.7, 143.5, 140.7, 130.4, 120.7, 120.5, 110.5, 107.4, 104.9, 57.7, 56.7, 41.5.

4-Methyl-4-aza-8,12-dioxatriangulenium tetrafluoroborate [1(b)]

To a solution of 4(a) (0.5 g, 1.05 mmol) in pyridine (3mL) was added pyridine hydrochloride (6 g). The reddish mixture was heated to 200°C for 2 h. The cooled residue was then dissolved in water. The product precipitated on addition of aqueous NaBF₄ solution (100 mL, 0.2 M). The precipitated material was filtered, washed thoroughly with water and diethyl ether and dried to get crude material. The crude material was triturated
several times with small volumes of DCM until the washings were nearly colorless. The material was crystallized from a mixture of acetonitrile and ethanol (1:1) by slow evaporation of solvent to yield red-orange crystals of $\text{1(O)}_2\text{(NMe)}$ (250 mg, 62%). $^1$H NMR (400 MHz, CD$_3$CN): $\delta$ 8.32 (t, $J$ = 8.5 Hz, 2H), 8.08 (t, $J$ = 8.5 Hz, 1H), 7.79 (d, $J$ = 8.7 Hz, 2H), 7.51 (d, $J$ = 8.4 Hz, 2H), 7.44 (d, $J$ = 8.4 Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-d$_6$): $\delta$ 152.1, 151.5, 140.7, 140.5, 139.71, 139.67, 111.5, 110.8, 109.1, 108.1, 105.1. The structure was confirmed by X-ray analysis.

Di-N-Methyl Dimethoxyphenylcarbenium tetrafluoroborate [5(a)]

Methylamine was bubbled for 5 min into NMP (25 mL) kept at 0°C. To this solution was added 3 (1.5 g, 2.94 mmol). After heating the red solution at 120°C for 2 h in a sealed tube, the reaction mixture was to cooled to room temperature. The reaction mixture was poured onto ice-cold water and acidified with HBF$_4$ solution (50% w/w aqueous, 0.5 mL) to get green-blue precipitate. The precipitated material was filtered, washed thoroughly with water and dried. The crude material obtained was triturated with EtOAc and DCM to get 5(a) (1.12 g, 86%). $^1$H NMR (400 MHz, CD$_3$CN): $\delta$ 8.19 (t, $J$ = 8.0 Hz, 3H) 7.92 (dd, $J$ = 8.7, 8.4 Hz, 2H), 7.49 (dd, $J$ = 8.7, 8.4 Hz, 4H), 6.95 (d, $J$ = 8.0 Hz, 2H), 4.11 (s, 3H), 3.75 (s, 3H).

4,8-Dimethyl-4,8-diaza-12-oxatriangulenium tetrafluoroborate [1(O)(NMe)$_2$]

A mixture 5(a) (0.5 g, 1.13 mmol) and pyridine hydrochloride (6.0 g) were heated to 200°C. After 3 h the reaction was cooled to room temperature and poured into ice-water.
Upon addition of aqueous NaBF$_4$ solution (15 mL, 0.2 M), the precipitate formed was collected by filtration. After thoroughly washing the precipitate with water and diethyl ether, the crude material was triturated with small amounts DCM until the washings were nearly colorless. The reddish material obtained was set for crystallization at room temperature by slow evaporation of a mixture of acetonitrile and N,N-dimethylformamide (DMF) to yield 1(O)(NMe)$_2$ (360 mg, 80%). $^1$H NMR (400 MHz, CD$_3$CN): $\delta$ 8.09 (t, $J = 8.5$ Hz, 1H), 7.90 (t, $J = 8.3$ Hz, 2H), 7.39 (d, $J = 8.9$ Hz, 2H), 7.28 (d, $J = 8.5$ Hz, 2H), 6.99 (d, $J = 8.3$ Hz, 2H), 3.67 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-d$_6$): $\delta$ 150.9, 139.9, 139.3, 138.9, 138.3, 137.4, 109.6, 109.4, 108.0, 105.9, 105.7, 35.2. The structure was confirmed by X-ray analysis.

9-(2,6-Dimethoxyphenyl)-1,8-dimethoxy-10-N-ethylacridinium tetrafluoroborate [4(b)]

Ethylamine was bubbled for 10 min into NMP (35 mL) cooled in an ice bath. To this solution was added 3 (2.5 g, 4.89 mmol). The solution was stirred in a sealed tube for 30 h at room temperature. The mixture was then poured into aqueous NaBF$_4$ solution (250 mL, 0.2 M) and acidified with HBF$_4$ solution (50% w/w aqueous, 1 mL). The precipitate was collected by filtration, washed with water and recrystallization from methanol to obtain dark-red crystals of 4(b) (1.17g, 48.6%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.21 (dd, $J = 8.1$, 8.1 Hz, 2H), 7.93 (d, $J = 9.1$ Hz, 2H), 7.35 (t, $J = 8.2$ Hz, 1H), 7.00 (d, $J = 8.0$ Hz, 2H), 6.65 (d, $J = 8.2$ Hz, 2H), 5.25 (q, $J = 7.3$ Hz, 2H), 3.55 (s, 3H), 3.54 (s, 3H), 1.88 (t, $J = 7.3$, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 160.8, 157.3, 155.6, 141.31, 140.4, 129.5, 119.9, 119.4, 108.9, 106.4, 103.5, 57.0, 56.0, 48.1, 13.35.
4-Ethyl-4-aza-8,12-dioxatriangulenium tetrafluoroborate [1(O)2(NEt)]

A mixture 4(b) (0.4 g, 0.81 mmol) and pyridine hydrochloride (6.5 g) were heated to 200°C. After 2 h the reaction was cooled to room temperature and poured into water. Upon addition of aqueous NaBF4 solution (15 mL, 0.2 M) and a few drops of aqueous HBF4 solution (50%), the precipitate was collected by filtration. After thoroughly washing the filtrate with water and diethyl ether, the crude material was purified by column chromatography over silica gel using methanol and chloroform for elution. The reddish material obtained from column was set for crystallization at room temperature by slow evaporation of acetonitrile to yield 1(O)2(NEt) (0.07 g, 22%). 1H NMR (400 MHz, DMSO-d6): δ 8.39 (dd, J = 8.3, 8.2 Hz, 2H), 8.12 (t, J = 8.5 Hz, 1H), 8.04 (d, J = 8.9 Hz, 2H), 7.63 (d, J = 8.9 Hz, 2H), 7.55 (d, J = 8.5 Hz, 2H), 4.89 (q, J = 7.1 Hz, 2H), 1.50 (t, J = 7.0, 3H). 13C NMR (100 MHz, DMSO-d6): δ 152.4, 151.6, 140.9, 140.0, 139.7, 139.6, 111.5, 110.4, 109.1, 108.4, 105.2, 43.6, 11.8. The structure was confirmed by X-ray analysis.

Di-N-ethyl diaza dimethoxy pherylcarbenium tetrafluoroborate [5(b)]

Ethylamine was bubbled for 10 min into NMP (20 mL) cooled in an ice bath. To this solution was added 4(b) (1 g, 2.04 mmol). After heating the solution to 100°C for 3.5 h in a sealed tube, the reaction mixture was cooled to room temperature. The reaction mixture was poured into water and to this was added aqueous NaBF4 solution (100 mL, 0.2 M).
The precipitated material was filtered, washed with water and dried. The crude material was mixed with methanol (20 mL) and aqueous HBF$_4$ solution (0.5 mL, 50%) and heated to reflux for 3 h. The reaction mixture was cooled to room temperature and poured into water. After addition of aqueous NaBF$_4$ solution (20 mL, 0.2 M), the precipitated material was filtered and dried. The crude material was further purified by column chromatography over silica gel using DCM and methanol as solvents for elution to yield 5(b) (425 mg, 44%). $^1$H NMR (400 MHz, CD$_3$CN): $\delta$ 8.19 (t, $J = 8.6$ Hz, 1 H), 7.91 (t, $J = 8.9$ Hz, 2 H), 7.58 (d, $J = 8.6$ Hz, 2 H), 7.52 (d, $J = 8.9$ Hz, 2 H), 6.93 (d, $J = 8.0$ Hz, 2 H), 4.78 (ddd, $J = 16.0$, 12.0, 8.0 Hz, 2 H), 4.56 (ddd, $J = 16.0$, 12.0, 8.0 Hz, 2 H), 3.74 (s, 6 H), 1.65 (t, $J = 7.4$, 3 H). $^{13}$C NMR (100 MHz, CD$_3$CN): $\delta$ 160.6, 143.4, 142.8, 139.7, 138.0, 137.5, 120.3, 113.9, 108.3, 105.6, 103.9, 56.5, 46.1, 12.1.

4,8-Diethyl-4,8-diaza-12-oxatriangulenium tetrafluoroborate [1(O)(NEt)$_2$]

A mixture 5(b) (0.4 g, 0.85 mmol) and pyridine hydrochloride (6 g) were heated to 200°C. After 3 h the reaction was cooled to room temperature and poured into water. Upon addition of aqueous NaBF$_4$ solution (15 mL, 0.2 M) the precipitate was collected by filtration. After thoroughly washing the filtrate with water and diethyl ether, the crude material was purified by column over silica gel using dichloromethane and methanol for elution. The reddish material obtained was left for crystallization at room temperature by slow evaporation of acetonitrile and methanol to yield 1(O)(NEt)$_2$ (70 mg, 80%). $^1$H NMR (400 MHz, CD$_3$CN): $\delta$ 8.22 (t, $J = 8.7$ Hz, 1 H), 8.05 (t, $J = 8.5$ Hz, 2 H), 7.52 (d, $J = 8.9$ Hz, 2 H), 7.44 (d, $J = 8.7$ Hz, 2 H), 7.25 (d, $J = 8.1$ Hz, 2 H), 4.52 (q, $J = 7.3$ Hz, 4 H), 1.50 (t, $J = 7.3$, 6 H). $^{13}$C NMR (125 MHz, DMSO-d$_6$): $\delta$ 151.7, 139.9, 139.7, 138.8, 138.7, 138.5, 110.9, 109.1, 108.1, 106.9, 105.6, 42.6, 10.8. The structure was confirmed by X-ray analysis.
N-Ethyl-N-methyl dimethoxyphenylcarbenium tetrafluoroborate 5(c)

Ethylamine was bubbled for 5 min into NMP (20 mL) kept at 0°C. To this solution was then added 4(a) (600 mg, 1.3 mmol). After heating the solution at 120°C for 90 min in a sealed tube, the reaction mixture was cooled to room temperature before pouring into aqueous HBF₄ solution (50% w/w aqueous, 1 mL). The precipitated blue-green material was filtered, washed with water and diethyl ether to get crude material that was further purified by column chromatography over silica gel using methanol and chloroform for elution to get 5(c) (285 mg, 49%). 

**1H NMR (400 MHz, CD₃CN):** δ 8.10 (t, J = 8.5 Hz, 1 H), 7.89 (m, 2 H), 7.51 (d, J = 8.7 Hz, 2 H), 7.42 (dd, J = 8.8, 8.5 Hz, 2 H), 6.91 (dd, J = 8.1, 2.7 Hz, 2 H), 4.76 (m, 1 H), 4.51 (m, 1 H), 4.05 (s, 3 H), 1.62 (t, J = 7.3, 3 H).

**13C NMR (100 MHz, CD₃CN):** δ 160.5, 160.0, 143.5, 142.9, 142.6, 140.3, 139.1, 138.1, 137.8, 137.2, 119.8, 113.7, 108.5, 108.2, 105.8, 105.3, 104.1, 104.0, 56.4, 46.0, 38.1.

4-Ethyl-8-methyl-4,8-diaza-12-oxatriangulenium tetrafluoroborate

[1(O)(NMe)(NEt)]

A mixture of 5(c) (0.26 g, 0.58 mmol) and pyridine hydrochloride was heated to 200°C for 2h. The reaction was cooled to room temperature and poured into water. Upon addition of aqueous NaBF₄ solution (10 mL, 0.2 M) and a few drops of HBF₄ solution (50% w/w aqueous), the precipitate was collected by filtration. The filtrate was washed thoroughly with water and diethyl ether. The crude material was further purified by
column chromatography over silica gel using methanol and chloroform for elution. The reddish material obtained from column was set for crystallization in a mixture of acetonitrile and DMF by slow evaporation of solvent at room temperature to get red crystals of \( \text{1}(\text{O})(\text{NMe})(\text{NEt}) \) (0.11 g, 46%). \(^1\)H NMR (400 MHz, DMSO-d\(_6\)): \( \delta 8.22 \) (t, \( J = 8.6 \) Hz, 1 H), 8.05 (t, \( J = 8.5 \) Hz, 1 H), 8.00 (t, \( J = 8.5 \) Hz, 1 H), 7.64 (d, \( J = 8.8 \) Hz, 1 H), 7.58 (d, \( J = 8.6 \) Hz, 1 H), 7.52 (d, \( J = 8.6 \) Hz, 1 H), 7.48 (d, \( J = 8.8 \), 8.5 Hz, 1 H), 7.25 (d, \( J = 8.1 \) Hz, 1 H), 7.19 (d, \( J = 8.1 \) Hz, 1 H), 4.51 (q, \( J = 7.1 \), 2 H), 3.86 (s, 3 H), 1.39 (t, \( J = 7.1 \), 3 H). \(^{13}\)C NMR (100 MHz, DMSO-d\(_6\)): \( \delta 151.6, 151.5, 140.8, 139.63, 139.5, 138.7, 138.53, 138.49, 138.3, 110.6, 109.5, 109.2, 108.1, 108.0, 106.8, 106.6, 106.0, 105.6, 42.6, 35.4, 10.9. \) The structure was confirmed by X-ray analysis.

\[ \text{4,8,12-trimethyl-4,8,12-triazatriangulenium tetrafluoroborate } \text{[1(NMe)_3]} \]

Methylamine was bubbled for 10 min into a solution of benzoic acid (6 g, 49 mmol) in NMP (15 mL) cooled to 0°C. To this solution was then added 3 (1 g, 1.96 mmol). After heating the solution at 200°C for 12 h in a sealed tube, the reaction mixture was cooled to room temperature before pouring into aqueous NaBF\(_4\) solution (100 mL, 0.2 M) and acidified with aqueous HBF\(_4\) solution (50%, 1 mL). The red precipitated was filtered, washed with water and diethyl ether to get crude material. The crude material was triturated several times with small volumes of chloroform, until the washings were nearly colorless, to get \( \text{1}(\text{NMe})_3 \) (530 mg, 66%). \(^1\)H NMR (400 MHz, DMSO-d\(_6\)): \( \delta 7.88 \) (t, \( J = 8.5 \) Hz, 3 H), 7.09 (d, \( J = 8.5 \) Hz, 6 H), 3.33 (s, 9 H). \(^{13}\)C NMR: could not be obtained due to very limited solubility.
Ethylamine was bubbled for 10 min into a solution of benzoic acid (6 g, 49 mmol) in NMP (15 mL) cooled to 0°C. To this solution was then added 3 (1 g, 1.96 mmol). After heating the solution at 200°C for 12 h in a sealed tube, the reaction mixture was cooled to room temperature before pouring into aqueous NaBF₄ solution (100 mL, 0.2 M) and acidified with aqueous HBF₄ solution (50%, 1 mL). The red precipitated was filtered, washed with water and diethyl ether to get crude material. The crude material was triturated several times with small volumes of dichloromethane, until the washings were nearly colorless, to get 1(NEt)₃ (370 mg, 42%). ¹H NMR (400 MHz, DMSO-d₆): δ 7.98 (t, J = 8.5 Hz, 3 H), 7.25 (d, J = 8.5 Hz, 6 H), 4.27 (q, J = 6.8 Hz, 6 H), 1.32 (t, J = 6.8 Hz, 9 H). ¹³C NMR (125 MHz, DMSO-d₆): 139.35, 139.27, 137.7, 42.17, 10.12.

A mixture of 3 (1 g, 1.96 mmol) and n-butylamine (4.8 mL, 3.58 mmol) in NMP (15 mL) was heated in a sealed tube for 24 h at 200°C. After cooling to room temperature the reaction mixture was poured into aqueous NaBF₄ solution (100 mL, 0.2 M) and acidified with aqueous HBF₄ solution (50% w/w aqueous, 1 mL). The red precipitate was filtered, washed with water and diethyl ether to get crude material. The crude material was purified by column chromatography over silica gel using methanol and chloroform as eluents to get 1(NBu)₃ (420 mg, 40%). ¹H NMR (400 MHz, DMSO-d₆): δ 8.04 (t, J = 8.5 Hz, 3 H), 7.25 (d, J = 8.5 Hz, 6 H), 4.27 (q, J = 6.8 Hz, 6 H), 1.32 (t, J = 6.8 Hz, 9 H).
Hz, 3 H), 7.33 (d, J = 8.6 Hz, 6 H), 4.31 (t, J = 6.9 Hz, 6 H), 1.74 (quint, J = 6.3 Hz, 6 H), 1.57 (sxt, J = 7.5 Hz, 6 H), 1.01 (t, J = 7.3 Hz, 9 H). $^{13}$C NMR (125 MHz, DMSO-d$_6$): 139.8, 139.7, 137.7, 109.8, 105.1, 46.8, 26.6, 19.3, 13.8.

5.2 Synthesis of anion

![Chemical structure of tetraphenylammonium 4,8-dioxo-4H,8H-dibenzopyren-12-oltae [2(O)$_3$]](image)

Tetrabutylammonium 4,8-Dioxo-4H,8H-dibenzopyren-12-oltae [2(O)$_3$]

The synthesis of anion, 2(O)$_3$, was achieved by a slight modification of the synthetic protocol developed by Bushby et al. $^{302}$ The only change from the original procedure involved use of Zn-Cu alloy in the reduction steps instead of sodium amalgam to avoid use of mercury. The crude material was crystallized from acetonitrile by slow evaporation of solvent at room temperature. The overall yield of the synthesis was about 6%. $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 8.74 (d, J = 7.5 Hz, 6H), 7.50 (t, J = 7.6 Hz, 3H), 3.12 (t, J = 8.0 Hz, 8H), 1.52 (m, 8H), 1.27 (m, 8H), 0.91 (t, J = 7.2 Hz, 12H); $^{13}$C NMR (100 MHz, DMSO-d$_6$): $\delta$ 180.5, 132.4, 132.3, 127.0, 120.3, 90.9, 57.5, 23.0, 19.2, 13.5.

5.3 Synthesis of salt pairs

![Chemical structures of synthesis of salt pairs](image)

4,8,12-trioxatriangulenium trioxytriangulenate [1(O)$_3$•2(O)$_3$]

A solution of 1(O)$_3$ (0.065 g, 0.17 mmol) in acetonitrile (35 mL) was added to a solution of 2(O)$_3$ (0.1 g, 0.18 mmol) in acetonitrile (30 mL). A dark green precipitate formed immediately was filtered, washed with acetonitrile, methanol, dichloromethane and
diethyl ether and dried to get \(1(O)_2 \cdot 2(O)_3\) (0.075 g, 71%). Due to low solubility, the NMR data could not be obtained. However, absence of peaks in \(^{19}\text{F NMR}\) and peaks due to alkyl groups of \(n\)-NBu\(_4\) in \(^1\text{H NMR}\) evidenced absence of the non-aromatic counter ions. MS (ESI): m/z 285 [Cation], 321 [Anion].

\[
\begin{align*}
\text{4-Methyl-4-aza-8,12-dioxatriangulenium trioxytriangulenate} \ [1(O)_2(NMe) \cdot 2(O)_3] & \\
\text{A solution of} \ 1(O)_2(NMe) (0.085 g, 0.21 mmol) \text{ in acetonitrile (80 mL) was added to a solution of} \ 2(O)_3 (0.115 g, 0.20 mmol) \text{ in acetonitrile (45 mL). A dark blue precipitate formed immediately was filtered, washed with acetonitrile, chloroform, ethyl acetate and diethyl ether and dried to get} \ 1(O)_2(NMe) \cdot 2(O)_3 \ (0.070 g, 54%). \text{Due to low solubility, the NMR data could not be obtained. However, absence of peaks in} \(^{19}\text{F NMR}\) \text{and peaks due to alkyl groups of} \(n\)-NBu\(_4\) \text{in} \(^1\text{H NMR}\) \text{evidenced absence of the non-aromatic counter ions. MS (ESI): m/z 298 [Cation], 321 [Anion].}
\end{align*}
\]

\[
\begin{align*}
\text{4,8-Dimethyl-4,8-diaza-12-oxatriangulenium trioxytriangulenate} \ [1(O)(NMe)_2 \cdot 2(O)_3] & \\
\text{A solution of} \ 1(O)(NMe)_2 (0.07 g, 0.17 mmol) \text{ in acetonitrile (60 mL) was added to a solution of} \ 2(O)_3 (0.1 g, 0.18 mmol) \text{ in acetonitrile (45 mL). A dark blue precipitate}
\end{align*}
\]
formed immediately was filtered, washed with acetonitrile, ethyl acetate, chloroform and diethyl ether and dried to get 1(O)(NMe)$_2$•2(O)$_3$ (0.085 g, 76%). Due to low solubility, the NMR data could not be obtained. However, absence of peaks in $^{19}$F NMR and peaks due to alkyl groups of $n$-NBu$_4$ in $^1$H NMR evidenced absence of the non-aromatic counter ions. MS (ESI): m/z 311 [Cation], 321 [Anion].

4,8,12-trimethyl-4,8,12-triazatriangulenium trioxytriangulenate [1(NMe)$_3$•2(O)$_3$]

A solution of 1(NMe)$_3$ (0.085 g, 0.21 mmol) in acetonitrile (80 mL) was added to a solution of 2(O)$_3$ (0.115 g, 0.20 mmol) in acetonitrile (45 mL). A dark blue precipitate formed immediately was filtered, washed with acetonitrile, chloroform, ethyl acetate and diethyl ether and dried to get 1(NMe)$_3$•2(O)$_3$ (0.070 g, 54%). Due to low solubility, the NMR data could not be obtained. However, absence of peaks in $^{19}$F NMR and peaks due to alkyl groups of $n$-NBu$_4$ in $^1$H NMR evidenced absence of the non-aromatic counter ions. MS (ESI): m/z 324 [Cation], 321 [Anion].
Appendix
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Synergy between π-interactions and electrostatics in Triangulene ion pairs, **Modekrutti, S.**; Cammers, A., ACS National Meeting, Fall 2012, Philadelphia, PA – Oral presentation

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