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Computational Studies of Ion Pairing. 10. Ion Pairing between Tetrabutylammonium ion and Inorganic Ions: A General Motif Confirmed

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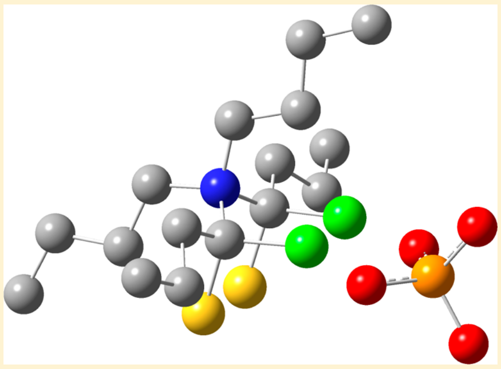
Supporting Information

ABSTRACT: Until recently, little has been known about the nature of the factors governing the stereochemistry of the interactions between organic ions, even though such information should be directly relative to issues of molecular recognition and supermolecular self-assembly. The present study of the preferred structures of the ion pairs between tetrabutylammonium and 22 common inorganic ions, a continuation of previous studies in this series, brings to 93 the number of such species that have been examined in this way. In every one of these ion pairs, the minimum energy orientation of the cation relative to the anion is the same, reinforcing the conclusion that this structural motif is completely general. This is the first such pattern to be identified for the mode of association between organic cations and polar species in solution.



INTRODUCTION

Increasing interest in molecular recognition and supramolecular assembly in recent years has created a need to know how chemical species recognize each other. If two species form a discrete complex, its structure can be readily determined by standard methods. How can we learn the structures of species such as ion pairs that form very weak complexes and thus by definition spend much of their time in solution as the individual species, associating only briefly before separating? Spectral methods are often good for establishing the existence of weak complexes but are ill-suited for establishing their detailed structures. Our long-time interest in the effects of ion pairing on electrochemical behavior[1,2] has evolved more generally into an interest in the structures of ion pairs between organic cations and anions in solution in organic solvents. The detailed structure of such ion pairs could provide valuable clues to the factors governing why one stereochemistry of association between two chemical species is preferred over another, i.e., exactly the same factors operating in molecular recognition. In light of the difficulty of establishing the structure of transitory ion pairs experimentally with any degree of precision, it has become clear in recent years that such information is best obtained by computational methods.[1,3] Our interest in the effects of ion pairing on electrochemical behavior of polycyclic aromatic hydrocarbons (PAH's) aroused our interest in the possibility of examining such effects by quantum chemical computations. These studies permitted us eventually to compute the experimental reduction potentials of a variety of polycyclic aromatic hydrocarbons (PAHs) with a high degree of accuracy and permitted evaluation of the separate contributions by the solvent and supporting electrolyte.[4,5] Our initial interest was primarily in computing the strength of the association constants between various tetraalkylammonium salts with PAH anions, but in the course of this work, we were excited by the unexpected yet chemically reasonable *structures* exhibited by these ion pairs.[1a,4−7] This confirms the expectation that ion pairing should respond to weak electrostatic interionic forces and thus that specific stereochemistries should be favored for ion pairs. The reasons why one mode of ion association is preferred should help in understanding the interactions between other organic and inorganic species. For these reasons, over the last several years we have carried out a series of computational studies on ion pairs between tetraalkylammonium salts and a variety of organic anions, including (a) dianions derived from PAHs[1a,4,5] and (b) nitrobenzene,[7a] nitrosobenzene,[7b] and a series of substituted benzaldehydes,[7b] each of these bearing charges ranging from zero to two and each of them ion paired to tetraalkylammonium cations (R_4N^+) with R ranging from ethyl through heptyl. In all, to date we have examined 73 such species. Prominently absent from this list have been inorganic ions, yet these ought to be even more likely than organic anions to form ion pairs since with fewer atoms, they often exhibit higher charge/size ratios, particularly when carrying charges greater than unity. We now report a computational study of both the strength of association and structure of ion pairs formed by association of the Bu_4N^+ ion with 22 common inorganic anions. The greater diversity of shapes among these anions contrasts with the largely planar benzenoid species we have treated previously, thus placing

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greater demands upon the stereochemistry of the ion pairing process.

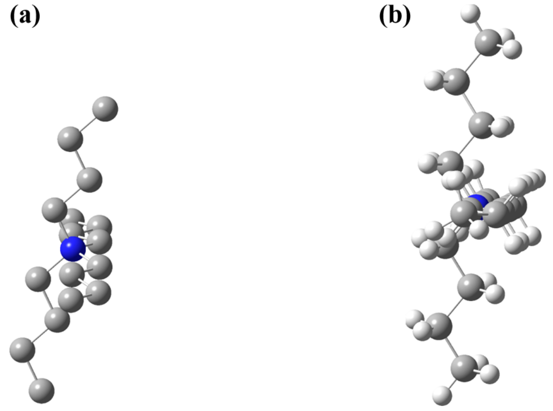
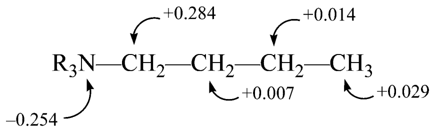


Figure 1. Tetrabutylammonium ion. (a) Left: view of extended carbon chains. (b) Right: carbon chains with hydrogen atoms added.



$$\mathrm{R_3\underset{-0.254}{N}{-}\overset{+0.284}{CH_2}{-}\underset{+0.007}{CH_2}{-}\overset{+0.014}{CH_2}{-}\underset{+0.029}{CH_3}}$$

Figure 3. Charges on nitrogen and groups in the tetrabutylammonium ion.

Stereochemistry of Ion Pairing of R_4N^+ Ions. It will be helpful to examine the stereochemistry of a typical all-organic ion pair before examining its inorganic counterparts. The lowest energy conformation of tetraalkylammonium ions (R_4N^+ where R is ethyl or longer) is of D_{2h} symmetry.[8] These ions are generally referred to as having a "pseudoplanar" geometry because the alkyl groups comprise two extended chains that lie in parallel planes (Figure 1). For the purpose of discussion, it is convenient to name the two chains "vertical" and "horizontal" as defined in Figure 1, where the vertical chain and horizontal chains are in the plane of, and perpendicular to, the plane of the paper, respectively. One might have reasonably expected that in the optimal structure of an ion pair formed by such a species with a benzenoid anion, the cation would be located above the plane of the benzene π-system (so-called cation−π "association").[9] We observed this previously to be the case for the ion pairs between tetraalkylammonium ions and the dianions of several polycyclic aromatic hydrocarbons.[4] However, we have also shown that when a polar substituent is attached to the ring, the substituent itself becomes the site of ion pairing and thus the cation is bound end-on and in the plane of the benzene ring.[1a,7,10] The computed structure of the ion pair between tetrabutylammonium ion and the anion radical of nitrobenzene[7] is shown in Figure 2. Note, by comparison with Figure 1, that in Figure 2 the horizontal chain is still perpendicular to the plane of the paper but the vertical chain is tilted such that the upper butyl segment of the vertical chain is above the anion. In this structure, the cation has in effect rotated clockwise around the axis defined by the horizontal chain. We refer to this orientation as the "tipped" geometry. It turns out that the computed structure of *every one of the other 72 ion pairs examined thus far exhibits this identical orientation* of the cation with respect to the anion.[1,7] What is so compelling about this geometry? Intuition might suggest that ion pairing should be driven by the attraction between the negative charge on the anion and the positive charge on the nitrogen atom of the ammonium ion. However, quantum chemical computations carried out at all levels of sophistication agree that while the overall charge on the cation is indeed +1, the nitrogen atom of the Bu_4N^+ ion actually carries a *negative* charge. The positive charge resides on its hydrogen atoms, and thus they are solely responsible for the attraction for the anion. Most of the net positive charge resides on the methylene groups α to nitrogen (Figure 3),[9−11] so these groups should dominate the electrostatic attraction for anions (the positive charge on the hydrogen atoms of each methylene group is larger than the negative charges on the carbon atoms). Returning to Figure 2, it can also be seen that the two hydrogen atoms shown in green on each side of the central nitrogen and in the horizontal chain are closest to the anion and hence most likely to interact with it. As a corollary of the tipping that brings these atoms closer to the anion, the hydrogen atoms shown in yellow are rotated away and too far from the arene to participate in ion pairing. Rather than point all four of the α-protons obliquely at the anion, it is apparently more energetically favorable to direct just two of them directly at the oxygen atoms of the anion. This is the driving force for the tipping phenomenon. Ion pair formation is almost completely due to the electrostatic attraction between the green α protons and the anion. The tetrabutylammonium ion contains 36 hydrogen atoms, but the ion pair owes its existence simply to these two. We therefore call them the "α-binding protons". The importance of the methylene protons α to nitrogen in association of alkylammonium ions with anionic species has been noted previously.[9,11] However, as far as we are aware, the facts that only one

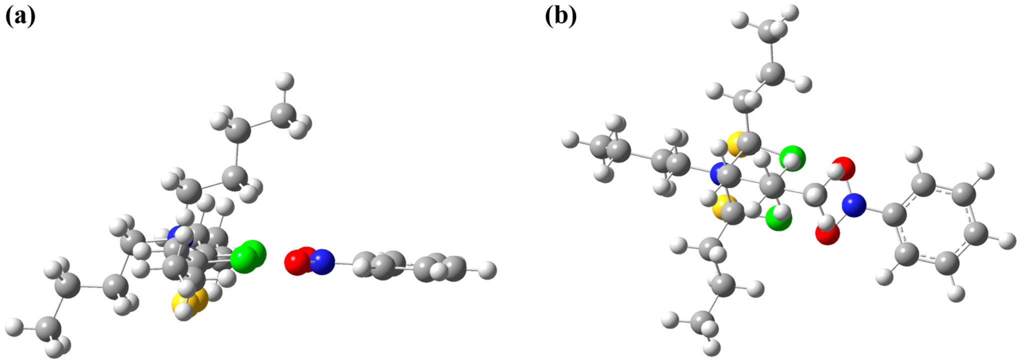


Figure 2. Ion pair between tetrabutylammonium ion and nitrobenzene anion radical. (a) Left: side view. (b) Right: top view.

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Table 1. Computed Association Constants for Ion Pairing between Tetrabutylammonium Ion and Common Inorganic Ions

entry	name	formula	geometry	$\Delta G_{\mathrm{assoc}}$ (kcal/mol)	$K_{\mathrm{assoc}}{}^{a}$
1	phosphate	PO_4^{3-}	tetrahedral	−3.902	730
2	carbonate	CO_3^{2-}	trigonal planar	−3.501	370
3	sulfate	SO_4^{2-}	tetrahedral	−3.404	310
4	hydrogen phosphate	HPO_4^{2-}	tetrahedral	−3.458	300
5	bisulfate	HSO_4^{-}	tetrahedral	−3.028	165
6	sulfite	SO_3^{2-}	tetrahedral	−2.958	147
7	fluoride	F^{-}	single atom	−2.764	106
8	dihydrogen phosphate	$H_2PO_4^{-}$	tetrahedral	−2.290	48
9	nitrate	NO_3^{-}	trigonal planar	−2.192	40
10	acetate	$CH_3CO_2^{-}$	trigonal planar	−2.126	36
11	bisulfite	HSO_3^{-}	trigonal planar	−2.111	35
12	chlorate	ClO_3^{-}	tetrahedral	−2.037	31
13	formate	HCO_2^{-}	trigonal planar	−2.021	30
14	perchlorate	ClO_4^{-}	tetrahedral	−1.948	26
15	methylmercaptide	CH_3S^{-}	linear; charge on a single atom	−1.810	21
16	nitrite	NO_2^{-}	trigonal planar	−1.810	21
17	tetrafluoroborate	BF_4^{-}	tetrahedral	−1.775	20
18	hexafluorophosphate	PF_6^{-}	octahedral	−1.743	20
19	hydrosulfide	HS^{-}	linear; charge on a single atom	−1.639	16
20	chloride	Cl^{-}	single atom	−1.348	10
21	perfluorotetraphenylborate (**1c**)	$(C_6F_5)_4B^{-}$	tetrahedral	−1.275	8
22	tetraphenylborate (**1d**)	$(C_6H_5)_4B^{-}$	tetrahedral	−0.993	5

[a] Data used to compute values of $\Delta G_{\mathrm{assoc}}$ and K_{assoc} are provided in Supporting Information.

hydrogen atom of each α pair is involved and that this gives rise directly to the tipped stereochemistry have not been pointed out in previous literature.

■ COMPUTATIONS

In the present study the structure of each ion pair was computed by the same density functional procedure using the Gaussian 09 suite of computational programs[12] that was used in two previous studies[1a,7] on the nature of ion pairing between tetraalkylammonium ions and neutral and anionic forms of nitrobenzene, nitrosobenzene, and a series of substituted benzaldehydes. Charges on the inorganic anions studied here vary between −1 and −3 depending on their structure, and the ion shapes vary between single atoms, tetrahedral, planar, and octahedral. The structure of each ion pair was established initially starting from several different orientations of the two components relative to each other through preliminary molecular mechanics geometry minimizations, followed by a second geometry optimization using a semiempirical (PM6) method. In all of the initial trial geometries the R_4N^+ cation was placed near the inorganic ion but several angstroms from it. A final optimization was carried out using the B3LYP functional with the 6-31G+d basis set, which includes diffuse orbitals (because one of the components of each ion pair carries a negative charge) and d orbitals on all first-row atoms. A functional that includes the effects of dispersion may be preferable to the B3LYP functional for obtaining ion pairing association constants. We expect to study the effect of other common functionals, e.g., M062X,[13a] including those including dispersion, e.g., the recent APF-D,[13b] in future work. Iodide and bromide ions were not included in this survey; iodine cannot be treated by the 6-31G+(d) basis set used in this and previous work, and in our previous experience energies of bromine species computed at this level are unreliable. Solvation energies of all species were computed by the polarized continuum method (PCM) of Tomasi,[14] assuming acetonitrile as solvent. Acetonitrile was chosen in our earlier work[1,7] because anions such as those from nitrobenzene and anthracene that are discussed there are frequently generated electrochemically in situ in an aprotic solvent of high dielectric constant, and acetonitrile is an excellent example of this. It is used in these computations for consistency with earlier work and to permit comparison with data in the literature. Charges on individual atoms in the ion pairs were computed by the Natural Population Analysis (NPA) method.[15] There is no generally accepted method for computing atomic charges, and in fact the concept of a localized atomic charge is ill-defined.[16] The values of the NPA charges have no intrinsic significance in our treatment, but we have found that the relative differences within sites in a molecule or the same sites in a group of related structures are generally informative. Free energies of association and association constants for ion pairing at 298 K (K_{assoc}) (Table 1) are defined as in eqs 1 and 2. They were computed in straightforward fashion from the computed free energies of the ion pair and its constituents. Energies of substances computed by the PCM method are free energies, simplifying the determination of $\Delta G_{\mathrm{assoc}}$. Computations such as these, involving the difference between the energies of two species, are generally found to be more accurate than the likely error in the energy of either component because of cancelations in errors in the computational method. The likely error in the computed ΔG for a reaction equilibrium can be estimated from the known likely errors in the experimental and computed energies of the reactants and products for a given computational method. Not only do the errors depend upon the computational method, this approach also requires that the method be tested upon a large set of known compounds. The most useful criterion of interest for a group of related compounds is the mean absolute deviation (MAD), defined as the average deviation between the absolute values of the difference between the computed and experimental values for each molecule in the model set. The MAD has been tabulated for a wide variety of computational methods.[17] For the equilibrium between a series of substituted 1,3,5-cyclooctatrienes and the corresponding bicyclo[4.2.0]-2,4-octadienes at the B3LYP/6-31G(d) level, we found an MAD of 0.98 kcal/mol for the computed ΔH,[18] even though the MAD for individual computations for this method is 7.9 kcal/mol.[17] The MAD of the B3LYP/6-31G+d method used herein is 3.9 kcal/mol;[17] we estimate the MAD for the ion pairing equilibrium (eq 1) as about half of 0.98 kcal/mol, or ±0.5 kcal/mol. Therefore, computed ion pairing association constants could differ within a factor of ±2.3 (antiln 0.5) of the experimental values. In fact, for all of the K_a's for which reliable experimental data are available (see below), the computed values do fall within this range.

$$\Delta G_{\mathrm{assoc}} = G_{\mathrm{assoc,computed}} - (G_{\mathrm{cation,computed}} + G_{\mathrm{anion,computed}}) \qquad (1)$$

$$\ln K_{\mathrm{assoc}} = \Delta G_{\mathrm{assoc}}/RT \quad (2)$$

■ RESULTS AND DISCUSSION

Ion Pairs between Bu_4N^+ and Inorganic Ions. The ions studied in this work (Table 1) in general represent many of the most commonly encountered inorganic anions of chemical practice. They were chosen to represent a diversity of charges and shapes and thus a greater potential variety of stereochemical outcomes. They include (a) single atoms or atoms bearing only hydrogen or alkyl groups, e.g., F^- and CH_3S^-, (b) planar trigonal species, e.g., NO_3^- and $CH_3CO_2^-$), (c) pyramidal ions, e.g., ClO_4^-, BF_4^-, and PO_4^{3-} or such species bearing just a hydrogen atom (HPO_4^{2-}, HSO_4^-), and an octahedral ion (PF_6^-). Certain of these species are unknown or not well characterized in the literature. For example, literature searches found only one reference to bis[tetrabutylammonium] carbonate in which it was used as a supporting electrolyte for voltammetry; it was implied without detail that the substance was a commercial sample.[19a] The 2:1 ion pair between tetrabutylammonium ion and monohydrogen phosphate has been prepared in situ in many studies by titration of phosphoric acid with 2 equiv of tetrabutylammonium hydroxide but used without further characterization.[19b]

Single Atoms and Related Species. (F^-, Cl^-, HS^-, CH_3S^-). The ion pairs of these anions with Bu_4N^+ cation are quite similar. The chloride and mercaptide species are typical (Figures 4 and 5). Note the distinctly tipped structure. In the ion pairs from the mercaptide and methyl mercaptide ions (Figure 5), the sulfur atom is closer than the methyl group to the cation; it carries a higher negative charge (−0.83) than the methyl (−0.15).

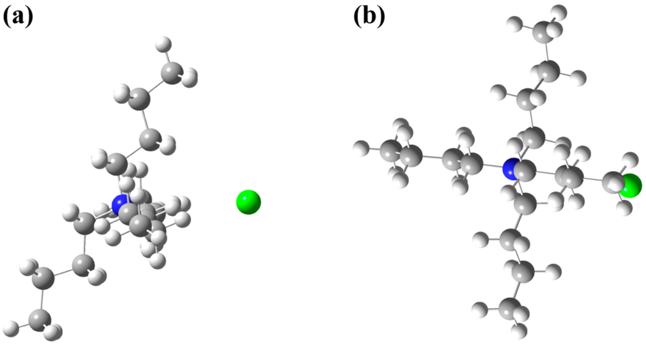

Figure 4. Ion pair between tetrabutylammonium and chloride ions. (a) Left: side view. (b) Right: top view.

Trigonal Planar and Related Species. (NO_3^-, NO_2^-, CO_3^{2-}, HCO_2^-, $CH_3CO_2^-$). These ions all form ion pairs in which two oxygen atoms are nearest the cation. A typical ion pair of this group of anions is that formed by the nitrite ion (Figure 6). The resemblance of this structure to that of the nitrobenzene anion radical (Figure 2) is clear. Both structures are tipped (the nitrite structure somewhat more so), and in both, the oxygen atoms of the anion point directly at the two α-binding protons. These features are common to all of the ion pairs of these trigonal planar species.

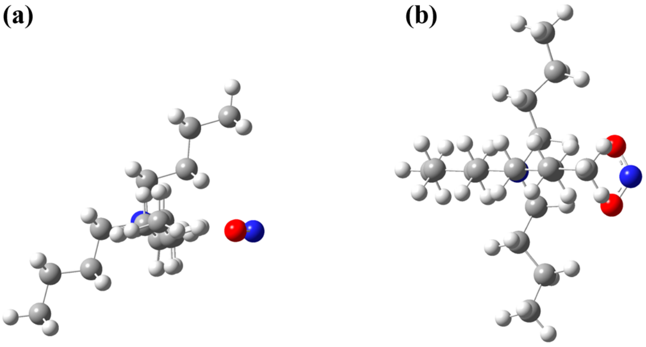

Figure 6. Ion pair between tetrabutylammonium and nitrite ions. (a) Left: side view. (b) Right: top view.

Tetrahedral Species (e.g., PO_4^{3-}, HPO_4^{2-}, HPO_4^-, ClO_3^-, and BF_4^-). These ions all exhibit two atoms directed at the α-binding methylene protons of the cation, though here the larger size of phosphorus does not permit as close a match (see top view) as in Figures 2 and 6. Note that in the tetrahedral ion pair with sulfite ion (Figure 8), the third oxygen atom on sulfur is directed upward toward the upper butyl chain, not downward; we found the same situation with a series of substituted benzaldhyde and nitrosobenzene anions and have argued that this is evidence that the β-methylene group of the upper chain plays a small but supplementary role in ion pair formation.[1a,6]

Octahedral Species. The only such species examined was the PF_6^- ion. Several minima were identified for this ion pair. The tetrabutylammonium ion is tipped in all of them, but the lowest energy geometry has two fluorine atoms of the anion directed toward the cation, once again in the tipped conformation (Figure 9).

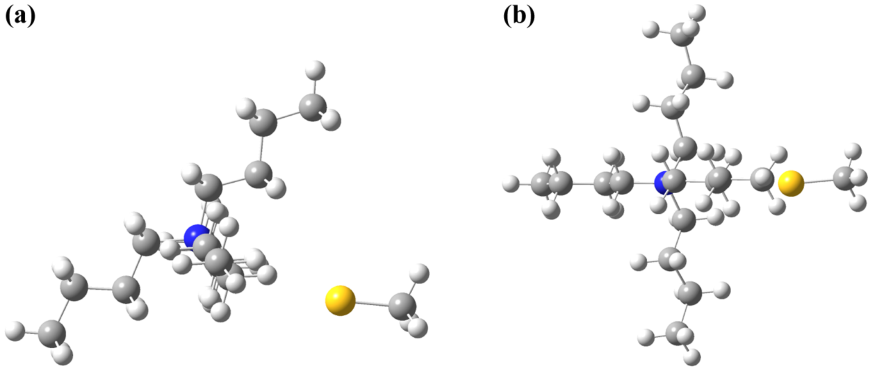

Figure 5. Ion pair between tetrabutylammonium and methylmercaptide ions. (a) Left: side view. (b) Right: top view.

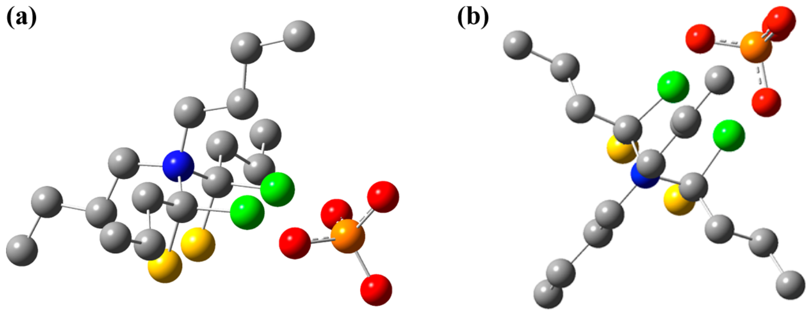

Figure 7. Ion pair between tetrabutylammonium and phosphate ions. Most hydrogen atoms removed for clarity. α-Binding hydrogen atoms in green. (a) Left: side view. (b) Right: top view.

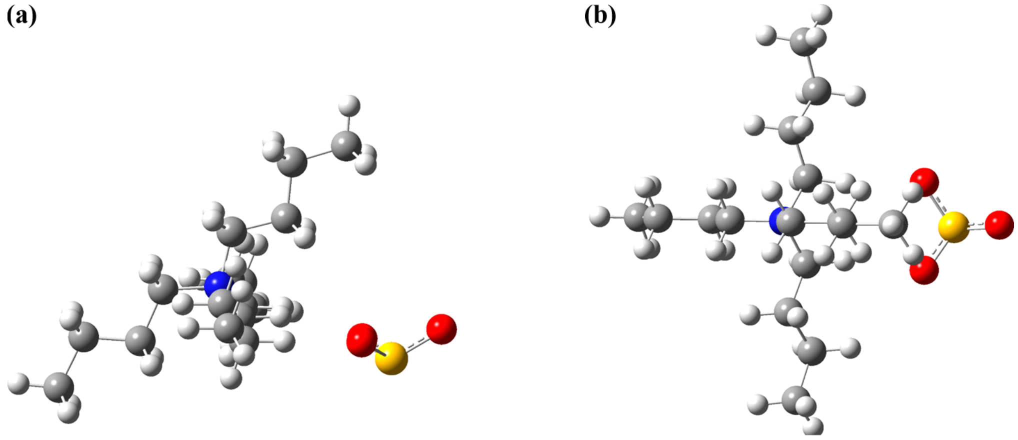

Figure 8. Ion pair between tetrabutylammonium and sulfite ions. (a) Left: side view. (b) Right: top view.

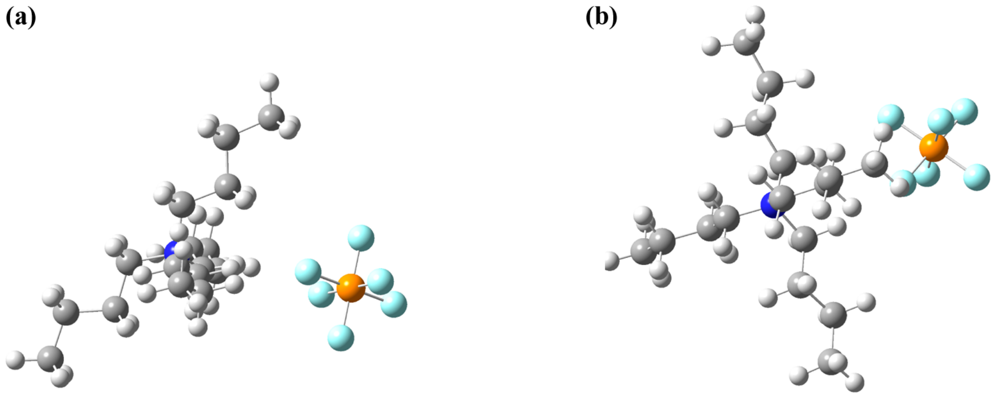

Figure 9. Ion pair between tetrabutylammonium and hexafluorophosphate ions. (a) Left: side view. (b) Right: top view.

Tetraarylborates $(C_6H_5)_4B^-$ and $(C_6F_5)_4B^-$. The last two species in Table 1 deserve comment. These tetrahedral anions do not form tipped ion pairs. The four aryl groups form a propeller-shaped shield around the boron atom that prevents a cation such as the Bu_4N^+ ion from approaching closely. Not only can the central boron atom not approach closely to the cation for steric reasons but the aryl groups have only C−H bonds or C−F bonds, no pair of which can be oriented directly at the α-binding protons. As a result, the cation is symmetrically disposed relative to the borate species (Figure 10).

A key element of the ion pairs of Figures 2 and 4 to 9 is the electrostatic attraction between the two α-binding hydrogen atoms of the ammonium cation and negatively charged atoms of the anion, achieved by tipping of the cation. As noted earlier, the most distinctive feature of the tipped geometry is that the two α-methylene protons (in green in Figures 2 and 7) point directly at the anion at the expense of their geminal neighbors. This is clearly evident in all of these structures. (A corollary of this is the overall C_{2v} geometry of the ion pairs; as seen in the top views, the ion pairs possess a plane of symmetry passing through the vertical carbon chain and the anion.)

Strength of Ion Pairing. The computed free energies of ion pair formation range from ca. −1 to −4 kcal/mol (Table 1), which is in the range to be expected for weakly associated species.[20] The ion pairing association constants clearly depend upon the degree of formal charge on the anion of interest. Note for example, the decrease of ΔG_{assoc} and K_{assoc} across the series PO_4^{3-}, HPO_4^{2-}, and $H_2PO_4^{3-}$. However, the ion pairing strength varies even for ions bearing the same charge (cf., sulfate and perchlorate). Generalizations based upon nucleo-

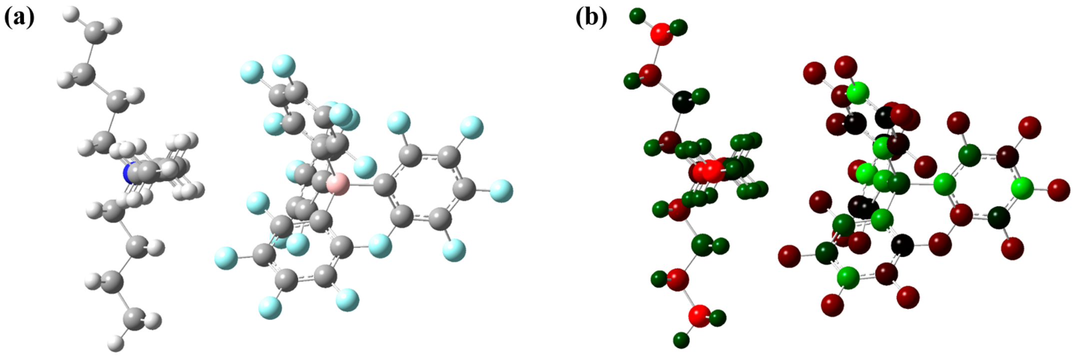

Figure 10. Ion pair between the tetrabutylammonium and tetrakis[pentafluorophenyl]borate ions. (a) Left: side view. (b) Right: charge distribution (bright red = highly negative; dark red = slightly negative; dark green = slightly positive; bright green = highly positive). Note the positive charge on boron.

philicity, such as softness or hardness[21a] of anions, are poorly correlated with K_{assoc}.[21b] Mercaptides are a good example of this: CH_3S^- and HS^- are excellent nucleophiles in, for example, S_N2 reactions but are computed to ion pair only weakly to Bu_4N^+ cation. Conversely, sulfate is a poor nucleophile yet has a large K_{assoc}. Krossing has also noted that his group has found no correlation with hardness or softness across a large number of ion pairs with weakly associating anions.[21c] This is not surprising, since nucleophilicity is related to the degree with which the anion can form a bond to an approaching electrophile, whereas ion pairing involves only electrostatic forces. Experimental measurements of free energies of ion pairing and association constants in the literature are sparse; hence, there is not a large body of data available with which to compare the computed values in Table 1.

Although a few other methods have been advocated,[22] almost all of the data for K_{assoc} of ion pairs in solution in the literature have been obtained by analysis of electrical conductance measurements as a function of electrolyte concentration. The data (see Supporting Information) exhibit much scatter. For example, reports of the K_{assoc} of tetrabutylammonium perchlorate (**1b**) and tetraphenylborate (**1d**) in acetonitrile range all the way from the conclusion that they are "fully dissociated" ($K_{assoc} \ll 0$) in this solvent to several recent values between 6 and 38. This is so despite the fact that most such studies of any given electrolyte in acetonitrile have measured the same conductance data for the solutions. The discrepancies actually arise from differences in the methods used by different investigators to carry out the computations required to extract K_{assoc} from the electrical conductance data,[16g,i,l] though it has also been shown that some data treatments do not yield a unique value of K_a.[23] The sophistication of these methods has improved over time, and in consequence, recent determinations, which tend to afford larger values, are probably more reliable. An important contribution was made by Barthel and co-workers,[24] who re-examined the original experimental conductance data from each of several earlier studies that had concluded that there is little or no ionic association in **1b** and **1d**. Applying a more contemporary data analysis, Barthel et al. came to the conclusion that both substances are substantially associated in acetonitrile (for example, K_{assoc} = 25 and 29 for **1b** and **1d**, respectively). Barthel et al. measured the K_a's of a number of well-studied ion pairs. In addition, where the original conductivity data were available from other studies, they recalculated the association constants using their more sophisticated procedure. Barthel's values are likely the most reliable values for K_a, since they were analyzed by the most recent software. Table 2 lists all of the literature data[22] that we consider reliable for the salts **1a−f** of Scheme 1. Except for **1c**, which seems to have been the object of only one study, only salts for which at least two measurements have been reported are listed in Table 2. In general, our computed ion pairing association constants are within a factor of 2 (see Computations) of the most recent literature values.

Table 2. Computed and Literature Experimental Association Constants (K_a) for Ion Pairing between Tetrabutylammonium Ion and Common Inorganic Ions in Acetonitrile

ion pair	computed K_a[a]	experimental K_a[b,c]
1a	20	12,[25a] 10,[25b] 13,[25g] 11[25j]
1b	26	10,[25c] 38,[25d] 15,[25g] 25,[24] 12,[25l]13,[25j] 25,[25h] 8,[25o] **24**(0),[25q] **20**(0)[25r]
1c	8	42[25d]
1d	5	5,[25c] **8**(28),[25e] 33,[25f] 29,[24] **11**(60),[25h] **6**(24),[25m] 5,[25r], **29**(0),[25p] **33**(14)[25r]
1e	10	24[25i]
1f	165	43,[22a] 63[25l]

[a] See Table 1. [b] Where two values are given, the first number in boldface is Barthel's recalculated K_a value from the original data; ref 24. [c] The second number in parentheses is the originally reported value.

Scheme 1. Ion Pairs Whose Asssociation Constants Have Been Reported (Table 2)

Bu_4N^+/X^-

1a, X = BF_4^-
b, X = ClO_4^-
c, X = $B(C_6F_5)_4^-$
d, X = $B(C_6H_5)_4^-$
e, X = Cl^-
f, X = HSO_4^-

A complication in comparing the computed and experimental data for association constants is the fact that some of the systems in Table 2 probably involve both solvent-separated and contact ion pairs. (It is generally assumed that conductivity arises only from the proportion of solvent-separated ions present in solution.) The K_{assoc} values reported in Table 1 are for pure contact ion pairs, because no additional solvent molecules have been explicitly included in the computations.

CONCLUSIONS

Ion pairing of the electrolyte cation to the electrogenerated anion causes a shift of the apparent reduction potential of conjugated systems to more positive potentials as measured by voltammetry.[4,5,25d,26] Voltammetric measurements in the absence of ion pairing should then provide a direct measurement of the reduction potential of a substrate in solution. Geiger has advocated the use of tetrakis[pentafluorophenyl]-borate salts, including **1c**, as electrolytes for this purpose[25d,26c] because not only are they highly hindered, but also the 20 fluorine atoms impart increased solubility, lower resistivity, and lower tendency toward adsorption on the electrode. We compute the Bu_4N^+ ion pair with **1c** to have a lower tendency to form ion pairs (K_{assoc} = 8.5) than any of the purely inorganic ions we have examined. The parent tetraphenylborate ion pair (**1d**) is computed to have a slightly lower K_{assoc} (5.4). The difference in ΔG_{assoc} between the two species is less than 0.3 kcal/mol, within the error of the computations.

Except for the tetraarylborates **1a** and **1b**, and irrespective of the shape of the anion, the Bu_4N^+ cation binds in exactly the same stereochemical fashion to all of these inorganic anions as it does with the organic anions we have previously studied. This brings to 93 the number of ion pairs that have adopted this common stereochemistry. The tipping phenomenon previously observed in ion pairs derived from anions as diverse as polycyclic aromatic hydrocarbons,[3] nitrobenzene,[6a] nitrosobenzene,[6b] and benzaldehyde and several substituted derivatives,[6b] is found with every one of the inorganic anion pairs studied in the present work as well. The tipped orientation of the tetraalkylammonium ion in these ion pairs, although eminently reasonable after the fact, could not have been predicted before the computations were carried out. Agreement over such a broad range of structures cannot be accidental. These results reinforce our confidence that tipping is a universal structural motif with tetraalkylammonium ions and indeed the first such motif to be identified. In future work we will report on structures of ion pairs formed from other organic cations of considerably different structure. Finally, comparison with the literature data in Table 2 suggests that ion pairing association constants can be determined by computation with accuracy comparable to that obtainable through conductance measurements.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Computed energies in Hartrees, and optimized coordinates and rotational constants of all species. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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