

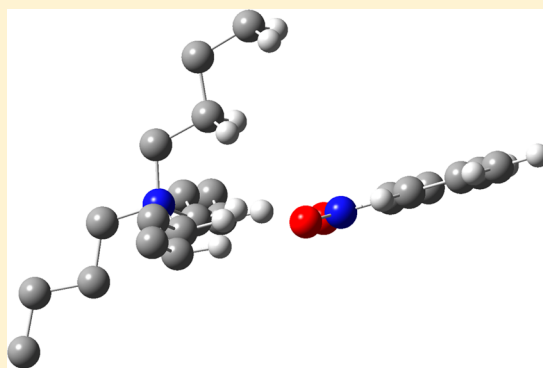
Computational Studies of Ion Pairing. 7. Ion-Pairing and Association Effects between Tetraalkylammonium Ions and Nitrobenzene Redox Species. "Ion Pairing" to Neutral Substances

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S Supporting Information

ABSTRACT: The structures of few ion pairs are known with any degree of certainty. In this work, the structures and energies of attraction in acetonitrile of nitrobenzene and its anion radical and dianion with a series of tetraalkylammonium ions of increasing size were computed by density functional theory. The resulting associated molecular pairs all exhibit the same unusual but chemically reasonable structure resulting from attraction between hydrogen atoms of the ammonium cation and the oxygen atoms of the nitro group. The cations form weak complexes with neutral nitrobenzene, stronger ion pairs with the monoanion, and strongly bound ion pairs with the dianion. The results delineate subtle issues governing the formation of such complexes that are directly relevant to issues of molecular recognition, self-assembly, and supramolecular chemistry.



■ INTRODUCTION

Ion-pairing interactions between organic cations and anions are important in any medium and particularly so in those of modest polarity. Electrostatic considerations suggest that the degree of ion pairing increases with decreasing dielectric constant of the solvent and with increasing charges on the constituent ions.² Since charged species are formed or destroyed in all electrochemical processes, ion-pairing is a frequent phenomenon in electrochemistry, particularly in organic solvents, of which even the most polar have much lower dielectric constants than water. Although ion pairing is ubiquitous in organic chemistry, there are no general experimental methods for determining the structures and association constants of organic ion pairs in solution. Indeed, the detailed structures of very few such species are known. Spectroscopic methods can often provide evidence for the occurrence of ion pairing in a given situation, but in general spectroscopy is not well suited for establishing chemical structures of ion pairs. NMR NOE measurements have occasionally provided useful structural information³ and in a rather limited application, structures of lanthanide ion pairs were determined by taking advantage of the NMR chemical shift, and relaxation rate effects were induced by lanthanide nuclei.⁴ It was suggested a number of years ago, however, that quantum chemical methods might represent a solution to this problem, and several examples were reported at that time.⁵ Indeed, several computational studies of the structures of ion pairs have been reported recently.⁶

We have been interested for some time in the use of computational methods to study the nature and degree of ion pairing in organic systems. These studies proved quite successful, for example, in providing a way to quantify the

separate effects of solvation and ion-pairing on electrochemical measurements.^{1a,c,f} This cannot be done by experimental methods, in which by their very nature solvation and ion-pairing always operate simultaneously. Our computational studies were originally carried out in an attempt to understand the puzzling effect of tetramethylammonium supporting electrolyte upon the voltammetric reduction of polycyclic aromatic hydrocarbons (PAH's) in organic media.^{7,8} This led to the discovery that tetramethylammonium ion exists completely as a bulky tetrasolvated species in strong donor solvents.^{1b,c} This was shown to account quantitatively for the unusual effects of this ion on PAH electrochemistry.^{1a} An unexpected benefit of this work, however, was the discovery that the computations also provided information on the *structures* of the ion pairs in addition to the strength of the association between the ions. The ion pairs between several PAH dianions and tetraalkylammonium ions were found to exhibit remarkably consistent structural motifs.^{1e} In fact, in every case we have examined, the structure of the ion pair can be seen to involve interactions that, though previously unsuspected, are nevertheless eminently chemically reasonable. We believe that computations are particularly well suited for the study of these evanescent species, and that further insights into the nature of nonbonded complexes will continue to come from computational approaches to ion pairing. The results are relevant to studies in areas involving nonbonded molecular interactions, such as

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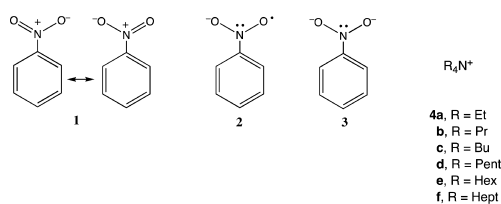
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molecular recognition, self-assembly, and supramolecular chemistry.

Our previous work focused on the interaction between tetraalkylammonium ions and PAH dianions because the voltammetric behavior of PAHs had supplied the experimental data⁷ by which we could assess the accuracy of our computational methods. The voltammetric behavior of PAHs in dimethylformamide, a relatively high polarity organic solvent, is affected by ion pairing of the electrolyte cation to the dianion but far less so to the hydrocarbon monoanion or parent hydrocarbon.^{7,8} This is reasonable since electrostatic theory suggests that the strength of a cation–anion interaction is proportional to the square of the charge on either ion.⁴ In a less polar solvent, even monocharged species can form ion pairs and even ion triplets to a significant degree, and this can have a significant voltammetric effect. We found this to be so in a study of the cathodic reduction of cyclooctatetraene in tetrahydrofuran containing a lithium salt as electrolyte.^{1d} Hydrocarbons carry no charge and therefore do not interact with the electrolytes used in voltammetric studies. But what are the effects of ion pairing on systems that carry charge even in the neutral form? Consider, for example, nitrobenzene (**1**), which is a hybrid of two structures in which each oxygen atom carries a formal $-1/2$ charge and the nitrogen atom carries a $+1$ charge (Scheme 1). It is well-known that nitrobenzene exhibits

Scheme 1



two successive one-electron reductions in aprotic media, first to the anion radical (**2**) and then to the dianion (**3**).⁷ It is not obvious how the charges on **2** and **3** might interact with the cation of a supporting electrolyte. Further, because of the permanent charges on the three atoms of the nitro group, it is not even clear whether or not the neutral parent (**1**) might itself interact with a charged component of the medium. As far as we are aware, this question has never been raised in the many literature studies⁹ of the voltammetric behavior of nitrobenzene and its derivatives. Since (a) electrochemical reduction of **1** in aprotic media is known to produce both **2** and **3** depending on potential, (b) the reduction is typically carried out in the presence of tetraalkylammonium (R_4N^+) salts, and (c) association between any or all of the species **1–3** and R_4N^+ ion might take place to a greater or lesser degree, it is clear that the thermodynamics of the first and second electron transfers, and hence the experimental voltammogram, could be greatly influenced by such interactions. In fact, we reported some time ago that the electrochemical behavior of 1,4-dinitrobenzene is greatly altered in an imidazolium ionic liquid, which ought to be especially prone to ion-pairing interactions.¹⁰ One may well ask whether the conventional description of the cathodic reduction of **1** in aprotic media as two one-electron transfers ought to be replaced by a more complex scheme involving interactions of the various nitrobenzene species with the cation of the supporting electrolyte, in which the association constants between the R_4N^+ ion and each of the species **1–3** would have to be explicitly taken into account. The present study is aimed

at learning the strength of such associations with several cations of varying size.

Computations. The energies of (a) nitrobenzene (**1**) and its corresponding anion radical (**2**) and dianion (**3**), (b) the six tetraalkylammonium ions (**4a–e**) ranging from ethyl through heptyl, and (c) all combinations of **1–3** with each of the R_4N^+ species were computed by density functional theory (DFT) with the widely used B3LYP functional^{12a} together with the 6-31G basis set with the addition of both diffuse orbitals and *d*-orbitals to the first row elements. The computations were carried out with complete geometry optimization using the Gaussian '09 suite of quantum chemistry programs.^{11a} [The tetramethylammonium ion was not included in this study because it bears a strongly held shell of solvent molecules in most common electrochemical solvents.^{1a–c} If nitrobenzene were then added to this structure, the combination would be a formidable computational problem because of its size and the large basis set used here to achieve high accuracy.] Solvation energies in acetonitrile (dielectric constant $\epsilon = 37.5$, chosen as a representative polar electrochemical solvent) were computed by the polarizable continuum method (PCM) of Tomasi.^{12b,c} The free energy of association, ΔG_{assoc} , is calculated as the difference between the free energy of the complex minus the sum of the free energies of the individual components. From this, the value of K_{assoc} at 25 °C can then be calculated. The ΔG_{assoc} and K_{assoc} values for all of the associated pairs are tabulated in Table 1; the computed free energies of all of the

Table 1. Energies and Properties of Pairs of Tetraalkylammonium/Nitrobenzene Species

entry	species	$\Delta G_{\text{assoc,calc}}$ (kcal/mol) ^a	$\Delta G_{\text{assoc,corr}}$ (kcal/mol) ^b	K_{assoc} (M ⁻¹)
1	Et ₄ N ⁺ /1	−0.93	−1.75	20
2	Pr ₄ N ⁺ /1	−0.79	−1.61	15
3	Bu ₄ N ⁺ /1	−0.87	−1.69	17
4	Pent ₄ N ⁺ /1	−0.93	−1.75	20
5	Hexyl ₄ N ⁺ /1	−0.61	−1.43	11
6	Hept ₄ N ⁺ /1	−0.61	−1.43	11
7	Et ₄ N ⁺ /2	−3.08	−3.90	730
8	Pr ₄ N ⁺ /2	−2.80	−3.62	450
9	Bu ₄ N ⁺ /2	−2.74	−3.56	410
10	Pent ₄ N ⁺ /2	−2.89	−3.71	530
11	Hexyl ₄ N ⁺ /2	−2.67	−3.49	360
12	Hept ₄ N ⁺ /2	−2.78	−3.60	440
13	Et ₄ N ⁺ /3	−4.74	−5.56	12020
14	Pr ₄ N ⁺ /3	−4.50	−5.32	8015
15	Bu ₄ N ⁺ /3	−4.40	−5.22	6770
16	Pent ₄ N ⁺ /3	−4.47	−5.29	7620
17	Hexyl ₄ N ⁺ /3	−4.05	−4.87	3750
18	Hept ₄ N ⁺ /3	−4.01	−4.83	3500

^aFree energies of association computed in CH₃CN by the DFT B3LYP/6-31+G(d)/PCM method. ^bAdditional $T\Delta S$ term of -0.82 kcal (2RT ln 2 at 298 K) added to $\Delta G_{\text{assoc,comp}}$ to account for the symmetry of ion pairing.

species (in hartrees) are given in the Supporting Information. (We prefer the terms “association”, “association constant”, and “associated pairs” as blanket terms to describe all of these interactions since “ion-pairing” is only appropriate for the interactions of **2** and **3** with **4**, whereas we regard **1–3** as actually representing a continuum of structures differing only in overall charge.) It should be noted that a more realistic picture

would include other geometries close in energy to the minimum. However, to this point, the only cations for which we have found multiple minima of similar energies are Et_4N^+ (see below) and the hypothetical bare Me_4N^+ ion, but as mentioned above, the bare ion does not exist in solutions of strong donor solvents.

Symmetry Effects on Ion-Pair Formation. Nitrobenzene and its monoanion and dianion are planar, and the symmetrical tetraalkylammonium ions **4** both have a pseudoplanar geometry (see below). Each of these components has two faces, either of which can engage in ion pairing. We encountered an analogous situation in our previous studies on the ion-pairing between tetraalkylammonium ions and polycyclic aromatic hydrocarbon dianions.^{1,5} This affects the equilibrium constants for ion pairing. For example, a species can ion pair to either face of nitrobenzene, increasing the rate of association by a factor of 2, whereas the ion pair can dissociate back to its constituents only one way. This has the effect of increasing the computed equilibrium constant for association K_{assoc} by a statistical factor of 2, thus adding a $T\Delta S$ entropic term equal to $RT \ln 2$ to $\Delta G_{\text{assoc,comput}}$. Since the same is true of the tetraalkylammonium ion, the overall effect is to increment the computed value of $\Delta G_{\text{assoc,comput}}$ by $2RT \ln 2$, or -0.82 kcal/mol at 298 K, and thus increase the association constant K_{assoc} by a factor of 4.¹³

RESULTS AND DISCUSSION

Structures of Ion Pairs and Complexes. In discussing the structures of tetraalkylammonium ions in which the alkyl chains are longer than methyl, it must first be appreciated that such ions do not have the approximately tetrahedral shape that intuition might suggest. The geometry around the central nitrogen atom is of course intrinsically tetrahedral, but steric interactions between the four groups attached to nitrogen cause the alkyl chains to exist preferentially in a pseudoplanar conformation containing two all-anti chains at right angles to each other in parallel planes, resulting in an overall D_{2d} symmetry for the ion (Figure 1).¹⁴ This has been recognized

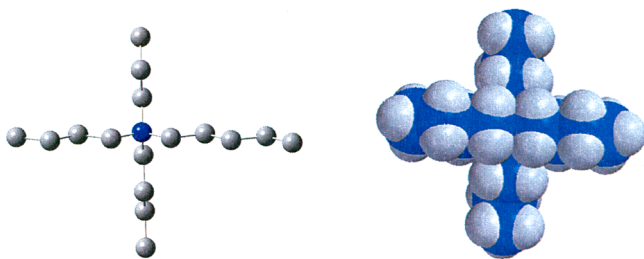


Figure 1. Tetraethylammonium ion in pseudoplanar conformation. (a) Left: carbon skeleton without hydrogen atoms. Right: space-filling model with hydrogen atoms added, showing the horizontal chain of methylene hydrogen atom pairs. A similar chain is on the rear (vertical) face.

for many years.^{14c} A second conformation of S_4 symmetry is known for tetraalkylammonium ions, but it is of higher energy.¹⁴ An important consequence of the D_{2d} geometry is the fact that the ease of approach to the center atom of the ion from above or below the pseudoplane is expected to be sterically relatively independent of the length of the alkyl chains. On the other hand, in their S_4 conformation, cations **4** behave sterically as globular species whose diameter and steric bulk increase substantially as the length of the alkyl groups increase. A second and we believe very significant consequence of the D_{2d}

conformation is that each face of the molecule presents a double row of methylene hydrogen atoms to any species approaching that face (Figure 1b).^{1e} Implications of this will be discussed below. For ease of subsequent discussion, the chain bearing this row will be referred to arbitrarily as “horizontal”, since it is shown in that orientation in Figure 1b; the other chain (on the rear face of the Bu_4N^+ pseudoplane in Figure 1b) will be referred to as the “vertical” chain. The rear chain has an identical but vertical row of hydrogen atom pairs; association may occur on either face.

Surprisingly, the structures of the various species resulting from association of tetraalkylammonium ions with **1–3** were found to be independent of the charge on the nitrobenzene moiety. The search for a minimum energy structure was initiated for each of the 18 pairs in Table 1 by placing the tetraalkylammonium ion in this orientation. This trial structure was then optimized by a molecular mechanics procedure. The tetraalkylammonium ion was always found to be located above the center of the aromatic ring at this stage. However, when the geometry was optimized by *any* quantum chemical procedure, i.e., semiempirical, Hartree–Fock *ab initio*, or density functional (DFT) methods, the cation moved to a new location in which the nitrogen atom of the cation lies near the nitro group on the end of the benzene ring almost in the plane of the ring and there is a plane of symmetry bisecting the ion and the benzene ring (Figure 2). The combination of tetrabutylammonium ion (**4c**) with nitrobenzene dianion (**3**) is shown in Figure 2, but this mode of orientation was actually found for *every one of the 18 pairs* in Table 1. Interestingly, if this new structure is again minimized by molecular mechanics, the cation returns to its original position above the aromatic system when $R = \text{ethyl}$ or propyl . The failure of the larger ions to return to the above-plane orientation may represent a stronger stabilization of the in-plane geometry. Situations where molecular mechanics and quantum chemistry give totally different structures are quite uncommon; usually, similar though not necessarily nonidentical structures are found. When a single-point computation (without geometry optimization) is carried out on the above-plane structure by any of the above-mentioned quantum chemical methods, its energy is always found to be much higher (10–40 kcal/mol) than the in-plane structure (Figure 2), demonstrating the latter to be the preferred structure in every case as well as the fact that the above-ring structure makes a negligible contribution. The Et_4N^+ ion is an exception to this statement and will be discussed below.

A notable feature of the 18 molecular pairs represented in Table 1 can be seen by further inspection of Figure 2. For purposes of clarity, most of the hydrogen atoms of the Bu_4N^+ group in Figure 2 have been deleted except for a set of eight, all of which are pointed toward the nitro group. Four of these are constituents of the “horizontal” row of methylene hydrogens, as defined in the preceding paragraph. The pair of methylene hydrogen atoms in the upper “vertical” chain and β to the nitrogen atom can be seen to point another two hydrogen atoms toward the nitro group. A second more distant pair from the terminal methyl group of the vertical chain is also directed somewhat toward the nitro group, but these hydrogen atoms are probably too far away to provide much electrostatic stabilization. *A priori*, one might have expected the pseudoplane of the tetraalkylammonium ion to be perpendicular to that of the nitrobenzene ring, by analogy to the well-known T-shaped benzene dimer.¹⁶ In fact, however, a striking feature

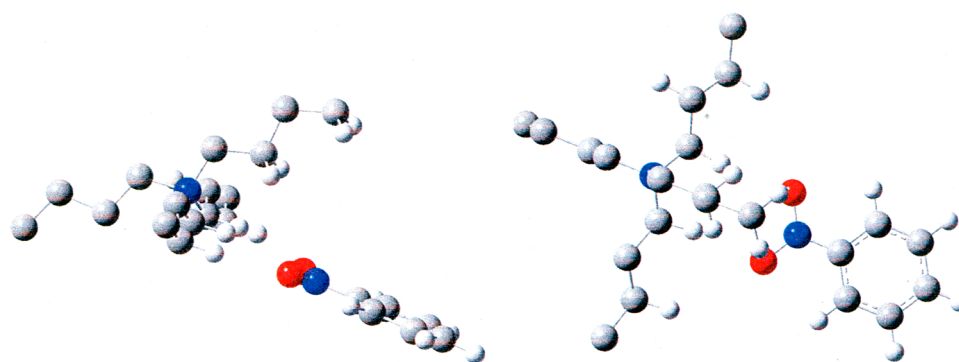


Figure 2. Computed structure of the tetrabutylammonium ion/nitrobenzene dianion pair in solution. (a) Left: side view, showing tipped orientation. (b) Right: top view. Only the hydrogen atoms of interest are shown.

exhibited by all of the tetraalkylammonium species from ethyl through heptyl is a pronounced tipping of the chain (by rotation about the axis of the so-called “horizontal” chain) such that the upper alkyl group of the “vertical” chain is brought nearer, and the lower chain further, from the nitrobenzene component. We found very similar tipped structures in the ion pairs of these same tetraalkylammonium ions with the dianions of several polycyclic aromatic hydrocarbons.^{1e} Ion pairs between arenulfonate ions and tetraalkylammonium ions also exhibit a similar row of hydrogen atoms in the cation pointed directly at the sulfonate oxygen atoms.¹⁵

The “tipped” orientation of the R_4N^+ cation in the ion pair arises because it presents a number of hydrogen atoms to the nitro group that represent a stabilizing contribution. Examination of the distribution of computed charges (Mulliken atomic charges) in the tetraalkylammonium ion reveals the fact that the carbon and nitrogen atoms carry a negative charge, whereas the protons carry a positive charge (Figure 3) and are thus

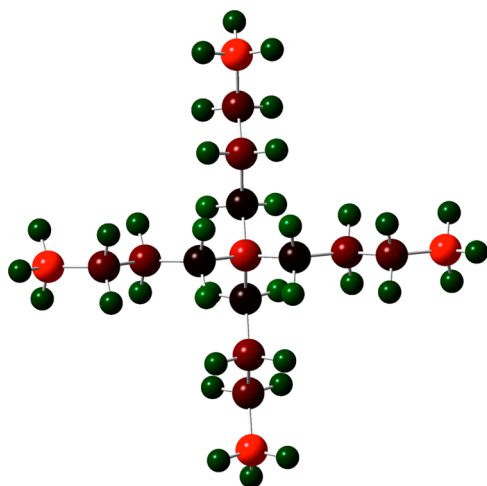


Figure 3. Tetraethylammonium ion, oriented as in Figure 1b, showing its charge distribution. Color code: bright red, highly negative; dark red, slightly negative; dark green, slightly positive.

primarily responsible for the electrostatic attraction between the two.^{11b} One might expect therefore that the association constants might increase with increasing alkyl group length as more such horizontal protons of the chain come into play pointing toward the nitro group. However, these additional protons are more distant from the nitro group and the electrostatic attraction between the two will be smaller.

Furthermore, the steric bulk of the alkyl groups also increases somewhat with chain length, which should decrease the association constant. It appears that the two opposing effects almost offset each other, resulting in the very modest observed decrease of K_{assoc} with increasing chain length in **4**. The decrease in K_{assoc} in going from **4a** to **4c** is less than a factor of 2, in sharp contrast to the behavior of the ion pairs of the same cations to polycyclic hydrocarbon dianions, which present a very different steric situation.^{1e} In point of fact, the center horizontal pair of methylene hydrogens flanking the nitrogen atom is the only one in a position to interact strongly with the oxygen atoms; as can be seen in the top view of the pair (Figure 2b), the other hydrogen atoms of the horizontal chain are not directed toward the nitro group, as well as being further away, and thus are not in a position to offer much stabilization of the negative charge on the hydrogen atoms.

Tetraethylammonium Ion. The tetraethylammonium ion **4a** is the only ion for which two orientations relative to the nitrobenzene component were found. The second structure (Figure 4b) lies 0.24 kcal/mol in energy above the tipped structure (Figure 4a) with **1** and 0.26 kcal/mol with **2** and **3**, indicating that about 1/3 of the pairs of Et_4N^+ with **1–3** have this geometry. As Figure 4b shows, only two such hydrogen atoms are pointed directly at the nitro group in the higher energy structure; they are directed at a single oxygen atom in the higher energy structure and lie in a plane perpendicular to that of the nitro group. The tipped structure (Figure 4a) has four hydrogens in the plane of the nitro group and they are interacting with both oxygen atoms. The fact that this structure is of lower energy is consistent with our argument that the principal cause of stabilization of these ion pairs is the electrostatic attraction between the positive charge on the hydrogen atoms of the cation and the negative charge on the oxygen atoms of the nitro group.

Strength of Association. The results in Table 1 demonstrate that the equilibrium constants for association of the nitrobenzene dianion (**3**)/ R_4N^+ pair (K_{assoc}) with the dianion **3** are quite large. However, quite unexpectedly, the computations predict that anion radical **2** forms ion pairs to a significant degree with R_4N^+ in acetonitrile, with its moderately high dielectric constant. In fact, even uncharged nitrobenzene associates weakly with these cations. The computed free energies of association of the cations ($\Delta G_{\text{assoc,comput}}$) with **1** are only about 1 kcal/mol. One might be tempted to dismiss this as within the computational error. However, if that were the case, one would expect the $\Delta G_{\text{assoc,comput}}$ values in the six species ranging from tetraethyl to tetrahexyl to be randomly distributed

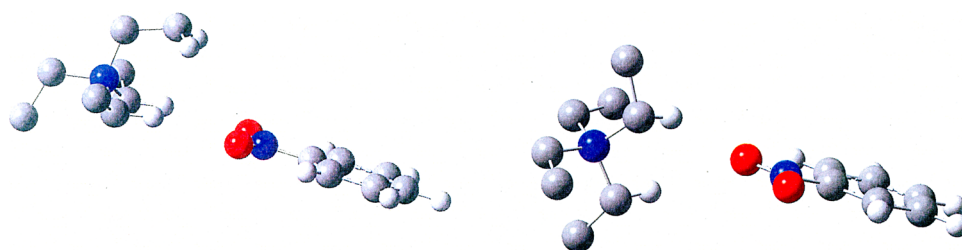


Figure 4. Tetraethylammonium ion complex with nitrobenzene. (a) Left: lower energy tipped orientation. (b) Right: higher energy nontipped orientation.

about zero rather than consistently negative. Furthermore, the computed structures of the associated structures of the neutral compounds are exactly the same as those found for the anions and dianionic species. Finally, it has repeatedly been established that errors tend to be minimized in computational studies of equilibria when, as we have, the same method is used to compute the energies of starting materials and products. This is because errors specific to the particular computational method employed are about the same on both side of the equation and tend to cancel.^{1a,17}

Our results show that nitrobenzene attracts tetraalkylammonium cations no matter what charge it bears. This is probably due to a combination of factors: (a) the oxygen atoms carry a substantial amount of charge in all of species 1–3, irrespective of the overall molecular charge, and (b) the charge in 1–3 is largely located on the two oxygen atoms of the nitro group. This can be seen, for example, in the electrostatic potential maps of 1–3 (Figures 5–7. ESR measurements have also

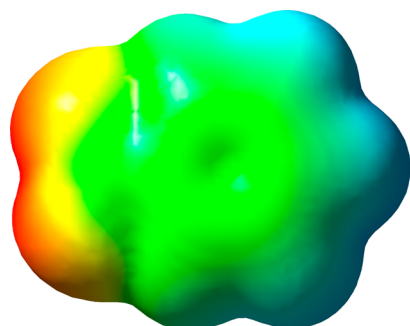


Figure 5. Electrostatic potential map of nitrobenzene (1).

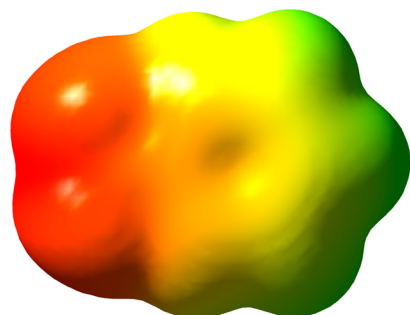


Figure 6. Electrostatic potential map of nitrobenzene anion radical (2).

demonstrated a high degree of electron localization on the nitro group in 2.¹⁸ As expected, the free energy of association increases dramatically with the charge on the nitrobenzene species but decreases with increasing size of the tetraalkylam-

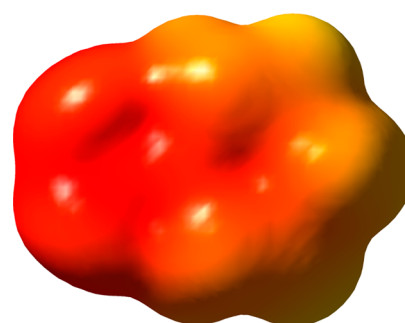


Figure 7. Electrostatic potential map of nitrobenzene dianion (3).

monium ion. However, the differences in K_{assoc} as one proceeds from ethyl to heptyl Et_4N^+ are remarkably small. As noted above, this is because of the pseudoplanar geometry of the R_4N^+ cations; sterically it is not much more difficult to approach the central nitrogen atom of R_4N^+ cations when R is heptyl than when it is ethyl.

Effect of Ion-Pairing to the Electrolyte Counterion. A counterion X^- will necessarily be present in any experiment in which species 2 and 3 are generated electrochemically. Reviewers of this manuscript pointed out that ion pairing of X^- to the tetraalkylammonium ion (4) is likely and raised the question of the effect of this upon the conclusions of this manuscript. Competition between two anions A and B for 4 can be treated in straightforward fashion, assuming that the two anions do not interact with each other. By definition, the association constants of A and B with 4 are $K_{\text{assoc,A}}$ and $K_{\text{assoc,B}}$, respectively, and are given by eqs 1 and 2, respectively. Denoting the respective ion pairs of A and B with R_4N^+ as $[\text{A}/\text{R}_4\text{N}^+]$ and $[\text{B}/\text{R}_4\text{N}^+]$

$$K_{\text{assoc,A}} = [\text{A}/\text{R}_4\text{N}^+]/([\text{A}][\text{R}_4\text{N}^+]) \quad (1)$$

and

$$K_{\text{assoc,B}} = [\text{B}/\text{R}_4\text{N}^+]/([\text{B}][\text{R}_4\text{N}^+]) \quad (2)$$

Recognizing that $[\text{R}_4\text{N}^+]$ must be the same in both equations

$$[\text{R}_4\text{N}^+] = [\text{A}/\text{R}_4\text{N}^+]/K_{\text{assoc,A}}[\text{A}] = [\text{B}/\text{R}_4\text{N}^+]/K_{\text{assoc,B}}[\text{B}] \quad (3)$$

thus,

$$[\text{A}/\text{R}_4\text{N}^+]/[\text{B}/\text{R}_4\text{N}^+] = (K_{\text{assoc,A}}[\text{A}])/K_{\text{assoc,B}}[\text{B}] \quad (4)$$

That is, the ratio of the concentrations of the two ion pairs is equal to the ratio of the products of the association constants for each species and the concentration of that species. $\text{Bu}_4\text{N}^+ \text{Cl}^-$ was chosen as a typical supporting electrolyte in organic electrochemistry. The association constant between Bu_4N^+ and

chloride ion was computed to be 19 using the same method as for the data in Table 1 (Supporting Information). Electrolyte and substrate concentrations are usually about 0.1 M and 1 mM, respectively, in typical electrochemical voltammetric experiments. Using the latter concentration values, one can estimate from eq 4 and data in Table 1 that, for example, that the respective ion pairs of Bu_4N^+ with nitrobenzene anion radical and chloride ion will be present in about a 1:5 ratio and that nitrobenzene dianion will be the major ion paired species (>3:1) in acetonitrile containing 0.1 M $\text{Bu}_4\text{N}^+/\text{Cl}^-$, even though chloride is in 1000-fold excess over the nitrobenzene species. More important is the stoichiometry: sufficiently free (not ion paired to chloride) Bu_4N^+ cation (about 5%) will be present in solution to engage in association with the organic anion, and because the concentration of the nitrobenzene species is much less than that of electrolyte, the computed K_{assoc} in Table 1 will not be significantly affected by the presence of chloride ion.

CONCLUSIONS

This study has established the same “tipped” structure for 18 nitro redox species/tetraalkylammonium ion pairs. This is surely not coincidental. We are confident that these represent the global minimum energy structures for such systems, providing good evidence for the notion that not only do ion pairs have a preferred geometry of contact but also that this geometry can be established by computation. The computed structures are generally chemically reasonable, involving interaction between the cation and the organic species which maximize the number of electrostatic interactions between the two. The “tipped” geometry exhibited by all of the pairs, while unexpected, achieves this maximization by locating one row of hydrogen atoms of the cation closer than the other, rather than locating the hydrogen atoms of both rows equidistant from the nitro group but further away. We found this feature to operate in the interaction of tetraalkylammonium ions with the dianions of polycyclic aromatic hydrocarbons,^{1e} presumably for precisely the same reasons.

As a consequence of the pseudoplanar D_{2d} conformation of the R_4N^+ cations and the resulting relative lack of steric hindrance to the central nitrogen even with the longest alkyl chains, their association constants with the nitrobenzene species 1–3 are almost independent of chain length, though highly dependent upon the charge on the nitrobenzene species. Unlike polycyclic hydrocarbons, where only the dianion forms ion pairs with the counterion, the radical anion and even neutral nitrobenzene both associate with tetraalkylammonium ions. Finally, the discovery that even neutral organic compounds and monoanions in which charge is highly localized can interact with tetraalkylammonium and presumably other cations has broad implications for the behavior of such species in the presence of charged species. For example, these interactions undoubtedly have a substantial effect on the voltammetric behavior of nitro, nitroso, and carbonyl compounds in aprotic media.⁹ Although the focus of the present work is upon a more general issue, i.e., the nature and strength of interactions of these cations with nitro groups carrying varied charges, we expect to take up the other issues raised by these results in future work.

ASSOCIATED CONTENT

Supporting Information

Computed energies in hartrees and optimized coordinates 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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DEDICATION

This manuscript is dedicated to the memory of Prof. Howard Zimmerman for his many contributions to physical organic chemistry.

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