JOC The Journal of Organic Chemistry

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Computational Studies of Ion Pairing. 8. Ion Pairing of Tetraalkylammonium Ions to Nitrosobenzene and Benzaldehyde Redox Species. A General Binding Motif for the Interaction of Tetraalkylammonium Ions with Benzenoid Species

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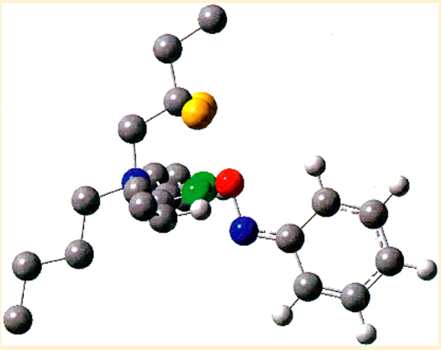
Supporting Information

ABSTRACT: Very little data is available on the detailed structures of ion pairs in solution, since few general experimental methods are available for obtaining such information. For this reason, computational methods have emerged as the method of choice for determining the structures of organic ion pairs in solution. The present study examines the ion pairs between a series of tetraalkylammonium ions and several redox forms of nitrosobenzene and a series of substituted benzaldehydes. The structures, though previously unexpected, are chemically reasonable and fit into a previous pattern of ion pairing described in previous publications in this series. To date in these studies, a total of 73 ion pairs and related species have in fact been identified having exactly the same unusual orientation of the tetraalkylammonium component with respect to the donor species. The results are pertinent to topics of general current interest, including self-assembly, molecular recognition, and supramolecular assembly.



INTRODUCTION

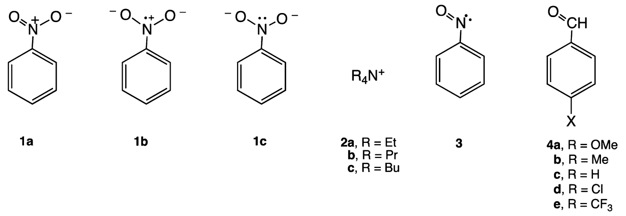
As we have noted elsewhere,[1] there are no good general methods for establishing the structures of ion pairs between organic cations and anions in solution. For this reason, there are very few organic ion pairs whose structure is known with any degree of confidence. Yet knowledge of how species prefer to contact and associate with each other in solution when at least one of them bears a charge would be important in view of the substantial current interest in issues of molecular recognition, supramolecular chemistry, and in general, self-assembly of complex systems. It has become increasingly clear in recent years that computational methods provide the best general method for determining the structures of ion pairs.[2] Our studies of ion pairing originally arose from a long-standing interest[4] in the effects of the medium upon the electrochemical behavior of unsaturated substances. The most prominent effects upon the reduction process, for example, which typically involves electrogenerated carbanions and dianions,[5] are ion pairing and solvation. The voltammetric behavior of a substance in an aprotic medium (measured as it must be in the presence of a supporting electrolyte) is usually found to be sensitive to the nature of the electrolyte cation and substrate, sometimes exquisitely so.[6,7] The dependence of the data upon the nature of the electrolyte cation arises because such experiments are typically carried out in polar aprotic organic solvents such as acetonitrile (AN), dimethylsulfoxide (DMSO), and dimethylformamide (DMF). Carbanions and dianions are highly reactive and hence demand the maximum stabilization from their environment. The most important stabilizing effect was suspected to be solvation, followed in importance by ion pairing of these species to the cation of the electrolyte. Several years ago, we began a computational study of these effects in order to assess quantitatively the relative contributions of solvation and ion pairing upon the behavior of anions generated electrochemically or otherwise.[8] While most of this stabilization was shown to come from solvation, ion pairing of the species to the cation of the electrolyte was found to play a significant role.[9,10] These studies provided convincing evidence that these phenomena can be treated quite well by quantum chemical computational methods.[7] It happened that there already existed good quantitative data[11] by which the validity of the computations could be assessed, and so our studies originally involved computation of the ion pairing strength, i.e., the association constant, K_{assoc} ,between dianions of polycyclic aromatic hydrocarbons (PAHs) and tetraalkylammonium cations in solution with them.[7−9] However, although this was the starting point for these studies, our attention was piqued by the very unexpected, yet still chemically reasonable, *structures* found for these ion pairs.[8,9] It was not all clear whether the structures found earlier for PAH dianion/tetraalkylammonium ion pairs[9] would be representative of ion pairs in general. For this reason, we recently examined another system, involving ion pairs between several nitrobenzene redox species (**1a**−**c**) and a series of tetraalkylammonium ions (**2**).[1] Chemical or electrochemical reduction is known to convert **1a** and other

Received: March 21, 2013
Published: April 30, 2013

nitroarenes to the corresponding anion radical (**1b**) and dianion (**1c**). The increasing charge on these species was expected to result in increasingly larger values of K_{assoc} between these species and **2** when proceeding through the series from **1a** to **1c**. Six symmetrical tetraalkylammonium ions (**4**) with R ranging from ethyl through heptyl were examined, resulting in 18 different combinations. As expected, the strength of association with a given tetraalkylammonium ion was found to increase with increasing charge on **1**, and K_{assoc} for a given redox form of **1** was computed to decrease with increasing chain length of **4**.

Interestingly, even though the structures of each of the resulting 18 associated pairs were optimized independently, *all 18 exhibited the same structure*, suggesting that a common cause underlies their association.[1] Nitrobenzene (**1a**) differs from the PAHs previously examined by us in that even though it is a neutral compound overall, its heteroatoms bear a permanent charge as seen by structure **1a**, with the oxygen atoms carrying partial negative charges and the tetraalkylammonium ion a positive charge. When **1a** is reduced by electron-transfer reagents or an electrode, the charge on oxygen increases in proceeding from **1a** through its anion radical **1b** to dianion **1c**, as seen in Scheme 1. We then considered what might then be expected for other molecules such as nitrosobenzene (**3**) and benzaldehydes (**4**) that, like nitrobenzene, can be written formally as neutral species with a ionic resonance contributor. Studies have shown that **3** and **4** can also be reduced to the corresponding anion radical and dianion redox states.[5] We now report the results of a study of the energies of association between cations **2a**−**c** and the neutral, singly, and doubly charged forms of both **3** and a series of substituted benzaldehydes (**4a**−**e**) (Scheme 1), chosen to provide a measure of substituent effects on K_{assoc}. The structures of the 47 resulting associated species are consistent with our previous studies on the corresponding nitrobenzene associated species **1a**−**c** but the pairs from nitrosobenzene and benzaldehydes exhibit certain distinctly different characteristics from the previously nitrobenzene species that shed further light on the association process.

Scheme 1



Computations. The computational procedure employed here was described in the previous paper in this series.[1] Initial structures were minimized by a molecular mechanics procedure, starting from several different starting geometries, followed by complete geometry optimization at the lowest of these at the density functional B3LYP/6-31+g(d) level. The association constant (K_{assoc}) for each 18 species is obtained in straightforward fashion from density functional computations of the respective free energies of (1) the six donor molecules (**3** or **4a**−**e**) in each of its 0, −1, and −2 redox states, (b) cations **2a**−**c**, and the various corresponding associated pairs.[1] A correction term is included to account for the entropy of mixing upon association of the two species.[12] This is necessary because the X═O bond can complex on either face of its π -bond, as can the pseudoplanar tetraalkylammonium ions[13] At 298 K, this entropy term favoring association is equal to $2RT$ ln 2, or −0.82 kcal/mol.[1,9] Computations were carried out using the Gaussian '09 suite of quantum chemical programs[3] with concomitant computation of solvation energies by the polarized continuum method of Tomasi.[14] Atomic charges were computed by the natural population analysis (NPA) method[15] subroutine in Gaussian '09.

RESULTS AND DISCUSSION

Association Constants between Tetraalkylammonium Ions and Nitrosobenzene and Aldehyde Redox Species. In this work, the structures and energies of the associated structures between the three tetraalkylammonium ions R_4N^+ (**2a**−**c**) and the neutral, anion radical, and dianion forms of nitrosobenzene (**2**) and five 4-substituted benzaldehydes (X = OMe, Me, H, Cl, and CF_3) in acetonitrile were computed. The computed association constants K_{assoc} of the resulting associated species could then be calculated from the computed energies of the individual components. The results are given in Table 1. Attempted computations on the ion pairs between the dianions of **4d** and **4e** were unsuccessful because these dianions appear to eject a halide ion spontaneously. We found a similar situation in earlier experimental work; attempted reduction of 4,4′-bis(trifluoromethyl)stilbene to the corresponding dianion using lithium in hexamethylphosphorus triamide resulted in products formed by initial ejection of fluoride ion.[16]

Table 1. Association Constants of Tetraalkylammonium/ArNX═O Pairs[a,b]

	K_{assoc} (M^{-1})					
species	3	4a	4b	4c	4d	4e
Et_4N^+/neutral	16	16	15	16	14	10
Pr_4N^+/ neutral	14	13	11	13	11	10
Bu_4N neutral	13	12	11	12	8	9
Et_4N^+/ anion radical	775	760	510	490	455	300
Pr_4N^+/ anion radical	570	530	430	300	260	215
Bu_4N^+/anion radical	520	440	360	300	215	200
Et_4N^+/ dianion	38290	19220	30890	21950	*c*	*c*
Pr_4N^+/dianion	16630	10390	16770	5780	*c*	*c*
Bu_4N^+/dianion	13160	7970	12850	6125	*c*	*c*

[a] Free energies of association computed in CH_3CN by DFT/B3LYP/6-31G+(d)/PCM method. [b] Additional $T\Delta S$ term of −0.82 kcal ($2RT$ ln 2 at 298 K) added to $\Delta G_{assoc,comp}$ to account for the symmetry of ion pairing. [c] Computations revealed that the dianion will spontaneously eject halide upon formation.

Structures of the Associated Species. The structures of the associated species formed between tetraalkylammonium ions and the various redox forms of nitrosobenzene (**3**) and the several substituted benzaldehydes (**4a**−**e**) have much in common with those formed by nitrobenzene yet with some distinct and significant differences. It will be helpful here to discuss first the structure of the previously determined[1] tetrabutylammonium ion/nitrobenzene dianion ion pair (Figure 1), which is identical to the other 17 related nitrobenzene species that we previously examined. Salient features of this structure are more readily seen in Figure 2, from which most of the hydrogen atoms have been removed and

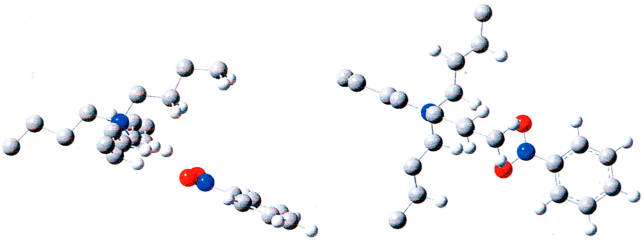


Figure 1. Side (left) and top (right) views of the ion pair between tetrabutylammonium ion and nitrobenzene (**1**) dianion.

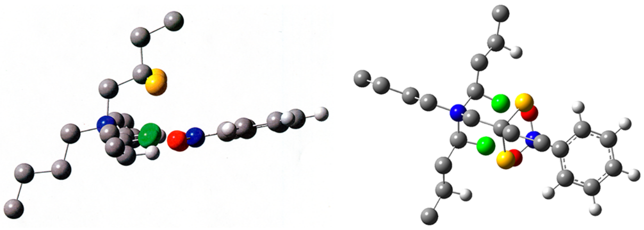


Figure 2. Side (left) and top (right) views of the ion pair between tetrabutylammonium ion and nitrobenzene (**1**) dianion. Left: side view. Right: top view. Color coding as described in the text.

others have been colored for ease of description. The significant features of this structure, which was described in more detail in our previous publication,[1] include the following: (a) as we reported, an extensive conformational search on ion pairs with nitrobenzene anions confirmed the previous conformational and X-ray evidence[13] that the global minimum geometry of the R_4N^+ ion (R = ethyl or larger) is the "pseudoplanar" conformation of D_{2h} symmetry, consisting of two chains lying in parallel planes and perpendicular to each other (Figure 3); (b) the D_{2h} conformation of these cations, when ion paired, lies several kcal/mol lower than any other conformation, an exception being the tetraethylammonium ion, in which a second conformation was found 0.24 kcal/mol higher than that of D_{2h} symmetry;[1] (c) two hydrogen atoms ((shown in green) α to the central nitrogen atom of one chain (which for convenience we refer to as the "horizontal chain"[1] of the Bu_4N^+ ion as shown in Figure 3) point directly toward the oxygen atoms of the nitro group and lie close to the plane of the nitrobenzene molecule; and (d) a second pair of hydrogen atoms β to nitrogen (shown in yellow) at the upper end of the "vertical" chain (again using our previously defined terminology) are also directed toward the oxygen atoms of the nitro group but from *above* the plane of the nitro group. We refer to this orientation of the tetraalkylammonium ion with respect to the second component, which brings the upper butyl group closer to the nitro group while the lower butyl group of the vertical chain is rotated away, as the "tipped" geometry. We suggested previously that the four hydrogen atoms in color are primarily responsible for the electrostatic attraction, which is maximal in the tipped structure, between the organic cation and the negatively charged oxygen atoms of the dianion.[1] This structure must have some particular advantages, since it was found for all 18 associated species between the six tetraalkylammonium ions from tetraethyl through tetraheptyl and the three nitrobenzene redox species (neutral, anion radical, and dianion).[1] With the nitrobenzene-derived structures in mind, we turn now to the structure of the ion pair between Bu_4N^+ and nitrosobenzene dianion (Figure 4).

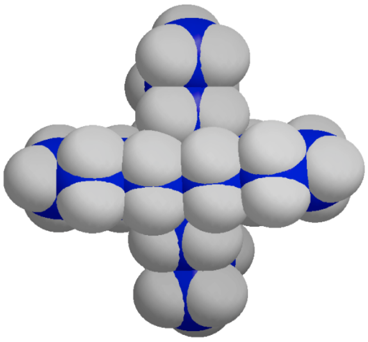


Figure 3. Space-filling model of Bu_4N^+ ion in a pseudoplanar conformation.

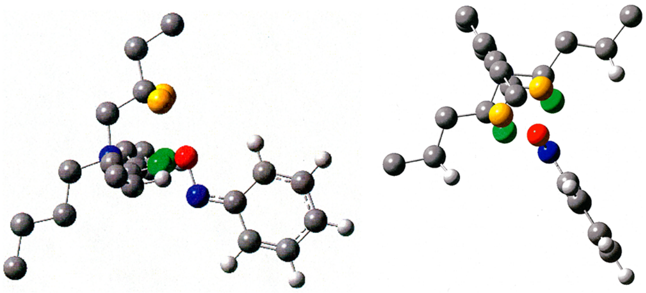


Figure 4. Side (left) and top (right) views of the ion pair between tetrabutylammonium ion and nitrosobenzene (**3**) dianion. Left: side view. Right: top view. Color coding as in Figure 2.

Comparison of Figures 2 and 4 reveals their similarity, particularly with respect to the tetraalkylammonium ion, suggesting that the factors responsible for ion pairing by the cation are the same in nitrosobenzene and nitrobenzene. However, the structures differ in an important respect: the plane of the aromatic ring is rotated 90° in Figure 3 compared with Figure 1. In fact this difference serves to validate the claim that the "upper" pair of hydrogen atoms plays a key role in the association process, because the sense of rotation is such that it brings the oxygen atom of the nitroso or formyl group closer to these hydrogen atoms, permitting their interaction and thus strengthening the degree of association between the two components.

Dependence of Association Constants upon Structure. Several features of the data in Table 1 deserve comment. The association constants between the tetraalkylammonium ions **2** and the redox species from neutral nitrosobenzene and its anion radical are similar in magnitude to those found earlier for nitrobenzene,[1] with K_{assoc} decreasing modestly as the length of the alkyl groups of **2** increase. Association constants for the dianion of nitrosobenzene are computed to be on average about twice as large as those of nitrobenzene. This is at least partly due to the fact that the negative charge, which is primarily responsible for the attraction between the two species,[1] is localized on a single oxygen atom in the nitroso dianions rather than being spread over two atoms in the nitro dianion, but as will be seen below, the geometries of the nitrobenzene and nitrosobenzene and aldehyde complexes are different, making comparisons difficult. The structures and association constants of the nitrosobenzene and benzaldehyde dianion ion pairs (see the following text) are also consistent with this conclusion.

Table 2. Natural Population Analysis Charges on the Atoms of the X═O Bond in Tetrabutylammonium/ArX═O Species Pairs

entry	ArX═O	X	charge on O	charge on X	overall charge on X═O
1	**3** neutral	N	−0.359	+0.079	−0.280
2	**4a** neutral	CH	−0.620	+0.564	−0.056
3	**4b** neutral	CH	−0.609	+0.572	−0.-037
4	**4c** neutral	CH	−0.601	+0.576	−0.025
5	**4d** neutral	CH	−0.596	+0.579	−0.017
6	**4e** neutral	CH	−0.584	+0.584	0.000
7	**3** anion radical	N	−0.650	−0.245	−0.895
8	**4a** anion radical	CH	−0.837	+0.269	−0.568
9	**4b** anion radical	CH	−0.824	−0.286	−0.538
10	**4c** anion radical	CH	−0.817	+0.291	−0.526
11	**4d** anion radical	CH	−0.805	+0.308	−0.497
12	**4e** anion radical	CH	−0.774	+0.344	−0.430
13	**3** dianion	N	−0.946	−0.434	−1.380
14	**4a** dianion	CH	−0.981	+0.159	−0.822
15	**4b** dianion	CH	−0.999	+0.123	−0.876
16	**4c** dianion	CH	−1.012	+0.109	−0.903
17	**4d** dianion	CH	*a*	*a*	*a*
18	**4e** dianion	CH	*a*	*a*	*a*

[a] Computations indicated that the dianion will spontaneously eject halide ion upon formation.

The association constants of ion pairs formed by nitrosobenzene anion radical and dianion are computed to be substantially larger than those for the corresponding benzaldehyde (**4c**) species. Inspection of the charges on the various species reveals the reasons for this (Table 2). First of all, their charge distributions differ. The oxygen atoms of the benzaldehyde species (neutral, anion radical, and dianion) actually carry a higher negative charge than do the oxygen atoms of the equivalent nitrosobenzene structures, from which might conclude that the benzaldehyde anions ought to form stronger ion pairs. However, carbon and hydrogen bear a positive charge in the benzaldehyde anions and this charge partially offsets the charge on oxygen, reducing the attraction of the formyl groups for neighboring tetraalkylammonium cations. Furthermore, our computations show that the nitrogen and oxygen atoms of nitrosobenzene *both* carry negative charge in the anions. Pilepic and Ursic have come to the same conclusion using a different computational method.[17] This group has also shown experimentally that nitrosobenzene exhibits nucleophilic reactivity at both nitrogen and oxygen.[18] The overall charges on the nitrosobenzene species are greater than those on the benzaldehyde formyl groups, from which one may conclude that nitrosobenzene and its anions should have a stronger attraction for nearby cations. In another sense, this can be seen as a manifestation of the "α effect", in which the nucleophilicity of an atom X: is enhanced when it is bound to a second atom Y also carrying an electron pair.[19] The electrostatic potential maps of nitrobenzene and benzaldehyde (Figure 5) clearly illustrate the higher electron density on the nitroso group of **3** compared to the formyl group of benzaldehyde (**4c**).

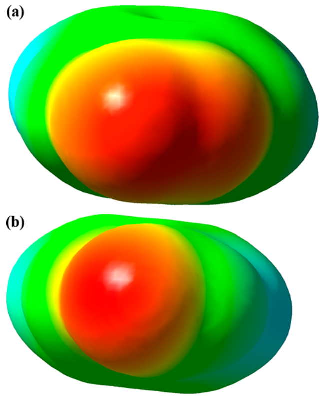
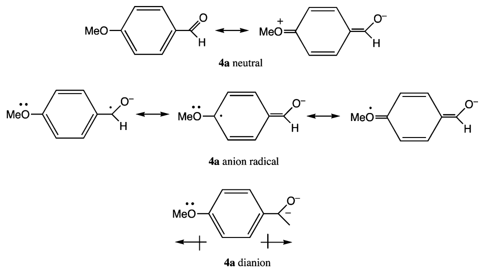


Figure 5. (a) Top: Electrostatic potential map of nitrosobenzene. The unshared electron pair (in red) is on the right. (b) Bottom: Electrostatic potential map of benzaldehyde. The hydrogen atom (in green) is on the right. The oxygen atom is on the left in both maps. Color coding: red, highly negative; yellow, slightly negative; green, slightly positive; blue, highly positive.

Certain aspects of the results on associations formed by the aldehydes (**4a**−**e**) are instructive. K_{assoc} is a measure of the nucleophilicity of the carbonyl oxygen atom toward those hydrogen atoms of the teraalkylammonium ion involved in the assocation process. K_{assoc} decreases smoothly across the series R = OMe, Me, H, Cl, CF_3 for both the anion radical and neutral species, in addition to the expected decrease with increasing length of the alkyl group.[1] However, the data of Table 1 also suggest that the situation is different with the dianion species; the computations appear to suggest that 4-methoxybenzaldehyde dianion is *less* nucleophilic than either benzaldehyde or 4-methylbenzaldehyde toward the cations **2**. We believe that this is a real effect rather than an anomaly of the computational method, for the following reasons. The carbonyl oxygen atom of neutral 4-methoxybenzaldehyde is a stronger base than benzaldehyde itself by a factor of more than an order of magnitude than benzaldehyde because of the well-established electron-donating resonance effect of the 4-methoxy group.[20] The importance of the resonance contribution of the unshared electron pair in neutral 4-methoxybenzaldehyde may also be seen by the fact, e.g., that rotational barriers in the BF_3 complexes of 4-substituted benzaldehydes,[21a] as well as the uncomplexed aldehyde,[21b] are correlated with Hammett σ^+, not σ. The anion radical of **4a** might also be stabilized through a similar extension of the ability of oxygen to stabilize a radical site at a benzylic position[22] However, in the dianion, the carbon and oxygen atoms of the carbonyl group are both forced to take on charge and cannot accept electrons from a remote group. Thus the 4−methoxy group can only be electron-withdrawing due to its intrinsically electronegative inductive and field[23] effects (Scheme 2). This analysis leads to the conclusion that the donor properties of this dianion should be of opposite

Scheme 2



nature than those of the neutral and anion radical species is supported by inspection of the NPA charges on the C−O atoms in the various benzaldehyde species. For both the neutral and anion radical forms, the charge on the aldehyde oxygen and the magnitude of K_{assoc} for the tetraethylammonium complex both steadily increase as the electron-donating power of the substituent increases as measured by the increasing negative charge on the carbonyl oxygen. In contrast, K_{assoc} decreases for the 4-OMe dianion, indicating that with this species, the group is *less* electron-donating than H or CH_3.

■ CONCLUSIONS

"Tipping" of Tetraalkylammonium Ions As a General Structural Motif. To date, in both this and previous work, we have found the tipped geometry in (a) 18 R_4N^+/nitrobenzene^x structures in which the charge x is equal to either −1, 0, or +1 and R ranges from ethyl through heptyl,[1] (b) nine similar combinations derived from nitrosobenzene, (c) 38 combinations derived from the series of substituted benzaldehydes **4a**−**e**, and (d) seven ion pairs between R_4N^+ ions and several polycyclic aromatic hydrocarbon dianions (Figure 6).[9] It cannot be a coincidence that these 73 structures are structurally so similar. They appear to represent a general binding motif of tetraalkylammonium ions toward electron donor species, in which the two hydrogen atoms in the horizontal chain (green in Figure 3) are carrying the brunt of the attractive force between the two species, with the upper (yellow) pair providing supplemental stabilization. On the other hand, all of the 73 structures are formed from planar (benzenoid) electron donor species. One might question whether nonplanar donor anions might behave similarly, for example. A more diverse range of candidates will have to be studied before it is possible to claim that the tipping phenomenon is a general structural motif for ion pairs between tetraalkylammonium ion and all electron pair (nucleophilic) donor species, and no doubt other modes of ion pairing will be observed with other types of cation. We are studying the structures and strength of association of ion pairs formed by more complex cations and donor species and will report the results at a later time.

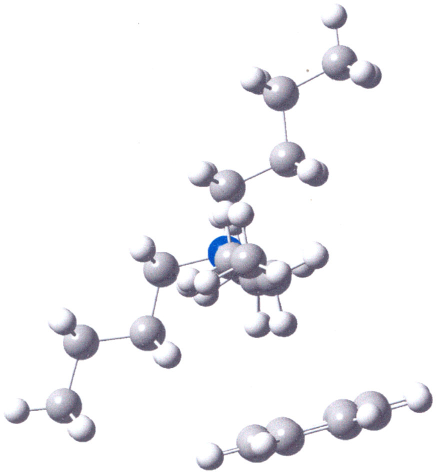


Figure 6. Ion pair between terabutylammonium ion and anthracene dianion showing tipping of the cation pseudoplane relative to that of the anthracene nucleus.

All 73 ion pairs (and the associated pairs in the case of the neutral species) from nitrobenzene, nitrobenzene, PAH dianions, and substituted benzaldehydes we have examined in this and our preceding report[1] contain the tetraalkylammonium subunit in its D_{2h} (pseudoplanar) conformation. Surely this too cannot be coincidental. In the unassociated ion the S_4 conformation is substantially populated at ambient temperatures. For example, the S_4 pseudotetrahedral conformation of the tetrabutylammonium ion appears to lie only about 1 kcal/mol above the D_{2h} in the isolated cation,[13] yet we have never found a complex in which the S_4 conformation is dominant; in fact, the only S_4 conformation that we ever have found is a tetraethylammonium ion pair with the various nitrobenzene redox species, where it constitutes only about 1/3 of the total.[1] We believe that the ion-pairing/association process enforces the D_{2h} geometry upon the tetraalkylammonium ion. Only this conformation permits *two* pairs of methylene hydrogens to participate in the interaction with the oxygen atoms of the other component. Pradines et al. have also noted that the energy spacing between the D_{2h} and S_4 geometries is greater than the uncomplexed R_4N^+ ion in the ion pairs formed between R_4N^+ ions and arenesulfonate ions.[24] The great preponderance of X-ray structures of salts containing the tetrapropyl- and tetrabutylammoniium ion exhibit these cations in their D_{2h} conformation as well.[13]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Computed energies in hartrees and optimized coordinates of all species. This information 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.

■ ACKNOWLEDGMENTS

Financial support was provided by Wesleyan University in the form of unlimited time on the Wesleyan High Performance Computer Cluster, which was financed in part by a grant from the U.S. National Science Foundation. This work was carried out during a sabbatical provided by Wesleyan University.

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