In conclusion, it can be said that, despite the limitations in the calculations discussed in this article and the previous article,[1a] the results of these investigations indicate that the observed fluorine hfs in aromatic radicals can probably be correlated with the two-parameter equation originally suggested by Eaton, *et al.*[3]

Ionic Interactions in Solution. I. Nuclear Magnetic Resonance Studies

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Abstract: Nmr spectra of numerous quaternary onium salts have been obtained in a variety of solvents. The magnitude of the solvent shift for a given ion in an aromatic solvent depends upon such factors as ion size and shape, solvent polarity, and the nature of the counterion. Our results are used to assess the importance of these factors in determining the extent of ion association and the nature of the associated species in solution. The experimental evidence suggests that both contact and solvent-separated species can form, with small ions in general forming more contact species.

The understanding of the nature of ionic solutions has been greatly extended through application of spectroscopic techniques. Use of absorption spectroscopy has facilitated differentiation between contact and solvent-separated ion pairs.[2] Information relating to ion pair geometries has been obtained through nmr studies of salts of transition metal complexes.[3] Recent spectroscopic and conductometric investigations have revealed that ion association in solution can be influenced by specific ion–solvent interactions which do not explicitly depend upon the dielectric constant of the medium.[4-6] A more thorough investigation of the importance of these interactions in determining the properties of ionic solutions would be desirable.

In proton nmr experiments the aromatic solvent induced shift (ASIS) experienced by polar molecules in aromatic solvents has been used to solve numerous structural problems.[7] As would be expected, the chemical shifts of ions dissolved in aromatic solvents are also strongly influenced by magnetic anisotropy effects. In this paper the ASIS experienced by a variety of cations and anions in low-dielectric aromatic solvents is examined, and the observed dependence of the ASIS on both ion–ion and ion–solvent interactions is discussed. These interactions are shown to depend on the size, shape, and charge density of the molecules involved.

Experimental Section

Nmr Spectra. Samples were run on a Varian A60-A spectrometer equipped with a variable temperature probe. Solvents, either reagent or spectroscopic grade, were obtained from the usual commercial sources, dried over molecular sieves (Matheson Coleman and Bell "Linde" Type 4A), and used without further purification.[8] Chemical shifts, recorded in hertz, were measured relative to internal tetramethylsilane (TMS, 1% v/v) by the usual side-band techniques and were in general reproducible to ±1 Hz. Downfield frequencies are shown as negative. Chemical shifts are taken as the centers of gravity of multiplets. Ion association had no observable effect on the ^{31}P–H coupling constant (~13 to 13.5 Hz).[9] All chemical shifts refer to α-methyl resonances unless otherwise specified. The estimated uncertainty in the quadrupole broadened resonance of the CH_3B group was ±2 Hz. Temperatures were measured using the Varian-supplied methanol or ethylene glycol samples. Most experiments were performed at probe temperature (40 ± 2°).

Preparation of Compounds. Quaternary onium salts were either purchased commercially or synthesized by standard methods.[10-12] When necessary they were recrystallized from suitable solvents.[10-12] Tetraalkyl- and tetraarylboron compounds were synthesized following Damico's general procedures.[13] Many of the tetraalkylboron compounds are air sensitive and subsequently were stored under nitrogen until they were used. New compounds and those whose melting points disagreed with literature values were checked by elemental analysis. Satisfactory results were obtained in all cases (Appendix).

Results

1. Cations. The α-methyl resonance frequency of methyl tributylammonium picrate is strongly solvent dependent (Table I). We ascribe these effects to cation solvation because the large differences in solvent shifts are not reduced at lower salt concentrations, indicating that ion association cannot be responsible. Reaction field[14] effects are apparently unimportant as there is

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[1] NSF Predoctoral Fellow, 1969–1970.

[2] L. I. Chan and J. Smid, *J. Amer. Chem. Soc.*, **90**, 4654 (1968), and references therein.

[3] R. H. Fischer and W. D. Horrocks, Jr., *Inorg. Chem.*, **7**, 2659 (1968), and references therein.

[4] (a) W. R. Gilkerson and J. B. Ezell, *J. Amer. Chem. Soc.*, **89**, 808 (1967); (b) A. D'Aprano and R. M. Fuoss, *ibid.*, **91**, 211 (1969).

[5] T. R. Griffiths and R. K. Scarrow, *Trans. Faraday Soc.*, **65**, 1427 (1969).

[6] S. Petrucci and M. Battistini, *J. Phys. Chem.*, **71**, 1181 (1967).

[7] P. Laszlo in "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. III, J. W. Emsley, J. Feeney, and L. N. Sutcliffe, Ed., Pergamon Press, London, 1967, Chapter 6.

[8] It is well known that commercially available 1-bromonaphthalene has a significant percentage of 2-bromonaphthalene. For the different sources of the solvent used in this study, the largest differences in observed shifts were about ±3 Hz. For critical comparisons, samples were prepared from the same bottle (Aldrich Chemical Co.) and the reproducibility in results was better than ±2 Hz.

[9] See also C. E. Griffin and M. Gordon, *J. Organometal. Chem.*, **3**, 414 (1965).

[10] G. M. Kosolapoff in "Organophosphorus Compounds," Wiley, New York, N. Y., 1950.

[11] J. B. Ezell and W. R. Gilkerson, *J. Phys. Chem.*, **72**, 144 (1968).

[12] A. Allerhand and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **85**, 1223 (1963).

[13] R. Damico, *J. Org. Chem.*, **29**, 1971 (1964).

[14] (a) A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960); (b) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

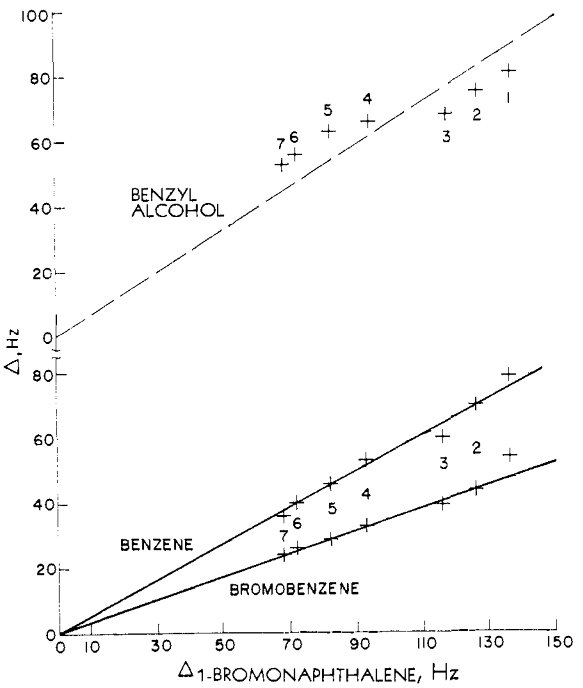

Figure 1. Comparison of solvent shifts for $CH_3N^+R_3X^-$ (0.02 *M*) in various aromatic solvents: abscissa, ASIS in 1-$C_{10}H_7Br$; ordinate, ASIS in other solvents (as labeled). Numbers correspond to same labeling scheme as in Table II.

no correlation between chemical shift and solvent dielectric constant.

Table I. Magnetic Resonance Frequency of $CH_3N^+(C_4H_9)_3Pic^{-\,a,b}$ in Various Solvents

Solvent	$-\nu$	Dielectric const[c]	Solvent	$-\nu$	Dielectric const[c]
$C_6H_5NO_2$	201	32.2	CH_3NO_2	184	34.2
C_5H_5N	196	12.0	*o*-$C_6H_4Cl_2$	173	9.5
$C_6H_5COCH_3$	196	17.0	CH_3CN	171	34.3
CD_3COCD_3	195	19.3[d]	C_6H_5Cl	162	5.4
C_6H_5CHO	194	15.0	C_6H_5Br	162	5.2
$CDCl_3$	191	4.5[d]	C_6H_6	145	2.2
CH_2Cl_2	187	8.0	$C_6H_5CH_2OH$	128	12.0
C_6H_5CN	187	24.0	1-$C_{10}H_7Br$	109	4.7

[a] Pic^- = picrate. [b] 0.02 *M*. [c] At 40°, estimated from data in A. A. Maryott and F. A. Smith, "Table of Dielectric Constants of Pure Liquids," National Bureau of Standards Circular No. 514, U. S. Government Printing Office, Washington, D. C., Aug 1951. [d] Dielctric constant of protonated compound.

Benzyl alcohol, chlorobenzene, bromobenzene, benzene, and 1-bromonaphthalene produce large upfield shifts. It is probable that the phenyl rings of these aromatic solvents interact with the cation in much the same way as they do with polar solute molecules. The electron-rich face of the aromatic ring is situated close to the positive charge on the central atom, thus placing the α-methyl group in a favorable position to experience a large upfield shift due to the diamagnetic anisotropy of the ring.[7,15] Those aromatic solvents which do not cause substantial upfield effects (*e.g.*, nitrobenzene, benzonitrile, etc.) must have a very different cation–solvent geometry. Probably the polar end of these molecules is in close proximity to the positive charge, and the aromatic ring is subsequently held either further from or at a different angle to the cation's α-methyl group. The observed behavior of the highly polar aromatic solvents toward cations parallels the effects of these solvents on polar solutes.[16,17]

Much of this work deals with low-dielectric aromatic solvents, and we will use deuteriochloroform ($CDCl_3$, dielectric constant = 4.5) as the reference solvent. Selection of a reference solvent of higher dielectric constant such as acetonitrile or methanol does not alter the discussion materially. We will return to the question of the choice of reference solvent and the significance of the results in nonaromatic solvents later.

The ASIS is defined in eq 1, where

$$\Delta = \nu - \nu_{CDCl_3} \tag{1}$$

Δ, the ASIS a given nucleus experiences in an aromatic solvent, is the difference between its magnetic resonance frequency in that solvent and in $CDCl_3$. A positive sign will indicate a shift to higher magnetic field. Though most of our results were obtained using 1-bromonaphthalene as the aromatic solvent, the same qualitative observations were made when bromobenzene or benzene was chosen (Figure 1). The hydrogen bonding capabilities of benzyl alcohol require special discussion (*vide infra*, Figure 1).

Ion Size Effects. We have measured Δ's for the series $CH_3N^+R_3X^-$ where R = alkyl and X^- = picrate or tetrabutylboride. For either anion, Δ decreases as the alkyl chain length increases (Table II and Figure 1).[18] The large chains probably act to increase the mean separation of positive charge and solvent. A similar but not identical trend was discussed by Schneider in his investigation of polar molecules in aromatic solvents.[15]

The α-methylene hydrogens of a given ammonium salt experienced Δ's approximately equal to the Δ of the corresponding α-methyl group. Hydrogens further from the positively charged heteroatom gave rise to smaller Δ's. This is to be expected as the active center is at the positive charge. The ring methyl resonances of the methyltritolylphosphonium salts in aromatic solvents also show this effect (Table III). The *ortho* methyl group, being closest to the positive phosphorus atom, experiences a larger shift than the *meta* or *para* ring methyls. The importance of the positive charge on phosphorus is clearly seen when the phosphonium results are compared with the ASIS's of the corresponding phosphines (Table III). The *meta* and *para* methyl groups of the phosphines experience a measurable ASIS while only slight effects are detectable in the case of the *ortho* group.[19]

Ion Association. Nonaromatic Solvents. In principle, the nuclear magnetic resonance frequencies of an ion should be independent of gegenion for a salt at infinite dilution in a given solvent. At moderate concentrations, however, the α-methyl resonance frequencies of a series of ammonium, phosphonium, and arsonium salts are anion dependent in many nonaqueous

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(15) W. G. Schneider, *J. Phys. Chem.*, 66, 2653 (1962).

(16) J. V. Hatton and R. E. Richards, *Mol. Phys.*, 5, 139 (1962).

(17) I. D. Kuntz, unpublished observations.

(18) The same trend is expected with most anions, but see discussion of "shielding" effects, below.

(19) Additional information concerning both ion–ion and ion–solvent interactions is provided in a consideration of the solvent effects on the α-methyl resonance frequencies of these salts (see below).

Table II. Chemical Shifts of Methyltrialkylammonium Salts $(CH_3N^+R_3X^-)^{a,b}$

R	Solvent $CDCl_3$ $-\nu$	 CH_3CN Δ^d	 C_6H_5Br Δ	 C_6H_6 Δ	 $C_6H_5CH_2OH$ Δ	 1-$C_{10}H_7Br$ Δ
(1) CH_3	202	19	54	79	81	136
(2) C_2H_5	185	15	44	70	75	126
(3) Quin^c	185	15	40	60	68	116
(4) C_3H_7	191	18	33	53	66	93
(5) C_4H_9	191	18	29	46	63	82
(6) C_5H_{11}	191	19	26	40	56	71
(7) C_6H_{13}	191	18	24	36	53	67

[a] 0.02 *M*. [b] X^- = tetrabutylboride for 1, 2, and 3; X^- = picrate for 4–7. [c] Quin = quinuclidinium, C_7H_{13}. [d] Although acetonitrile is not aromatic, we show Δ for comparison with aromatic solvents.

Table III. Ring Methyl Magnetic Resonance Frequencies of Tolyl Phosphonium Salts $(CH_3P^+(PhCH_3)_3X^-)^a$

	Solvent $CDCl_3$ $-\nu$	 1-$C_{10}H_7Br$ Δ	 $C_6H_5CH_2OH$ Δ
X^- = Iodide			
ortho	145	55	38
meta	150	36	26
para	149	45	22
X^- = Picrate			
ortho	142	67	36
meta	145	36	22
para	149	42	21
Ring Methyl Resonances of Triaryl Phosphines $(P(PhCH_3)_3)^a$			
ortho	142	−4	0
meta	136	16	15
para	138	16	13

[a] 0.05 *M*.

Table IV

A. Chemical Shifts of Methyltriphenylphosphonium Salts $(CH_3P^+Ph_3X^-)$

	Solvent $C_6H_5NO_2$ $-\nu$	 C_6H_5CN $-\nu$	 $CDCl_3$ $-\nu$	 CH_2Cl_2 $-\nu$	 CH_3NO_2 $-\nu$	 CH_3OH $-\nu$	 CH_3CN $-\nu$
			Salt Concentration, 0.05 *M*				
X^- = Cl^-	209	204	203	197	179	179	175
X^- = Pic^-	187	177	182	174	176	179	169
Difference	22	27	21	23	3	0	6
			Salt Concentration, 0.004 *M*				
X^- = Cl^-	189	195	206	196	177	179	169
X^- = Pic^-	185	175	185	173	176	179	169
Difference	4	20	21	23	1	0	0

B. Chemical Shifts of Onium Salts in $CDCl_3(CH_3M^+R_3X^-)^a$

	Cl^-	Br^-	I^-	Pic^-	CH_3B^-(cyclohexyl)$_3$
$CH_3N^+(C_4H_9)_3$			198	191	186
$CH_3P^+(C_4H_9)_3$			127	120	115
$CH_3P^+Ph_3$	203	200	194	182	(172)^b
$CH_3As^+Ph_3$	199	197	193	180	(170)^b

[a] 0.05 *M*. [b] Compound decomposed in $CDCl_3$; resonance frequency estimated from trends observed for other salts; estimated uncertainty ±3 cps.

solvents (Table IV).[20] In general, the smaller the anion, the more downfield is the cation. Ion association must be responsible for these effects. The chemical shift differences are functions of salt concentration, being reduced at lower concentrations. The nmr evidence indicates however that at the lowest concentrations the salts are still considerably associated in most of the solvents studied (Table IVA). The results should reflect differences between the anions with respect to (a) their ability to associate with cations and (b) the electric fields they produce in the associated species.

Ion Association in Aromatic Solvents. "Shielding" of Cations by Anions. Anion effects are greatly magnified in 1-bromonaphthalene (Table V). The magnitude of Δ is dependent upon anion size, a more upfield shift being associated with a larger anion. The magnitude of Δ in aromatic solvents should reflect a time averaged geometry between cation and solvent molecule. The very sizable cation shifts observed with large anions (*e.g.*, CH_3B^-(cyclohexyl)$_3$) suggest that the cation–solvent interaction is relatively unhindered. To explain the much smaller Δ's with other anions we postulate that ion association in 1-bromonaphthalene places the anions in close proximity with cations, thus preventing close approach between cations and solvent molecules.[21] Anions thus "shield" cations from the solvent, the smaller anions being more efficient at displacing solvent molecules.[22] The relative "shielding" abilities of anions are approximately independent of cation and salt concentration (~0.25 *M* to 0.005 *M*, *e.g.*, see Figure 2).

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(20) The major exceptions appear to be good proton donors such as methanol (see below).

(21) It is possible that in the associated species the anion changes the preferred orientation between cation and solvent molecule, but we believe it is unlikely to be a large effect unless cation and anion are very close together (see Discussion).

(22) The arsonium halides were heated to dissolve them in 1-bromonaphthalene. The evidence suggests that they decomposed.[23]

(23) R. Taylor, unpublished observations.

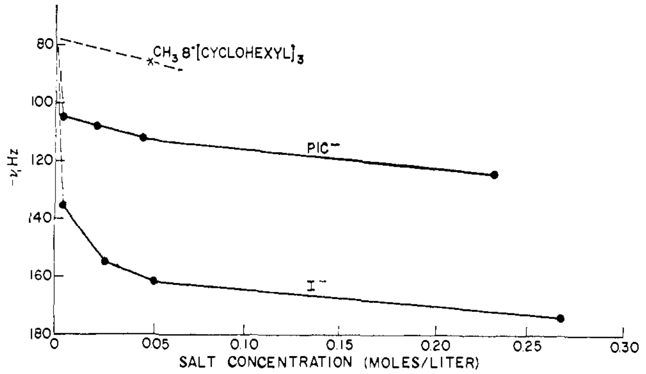

Figure 2. α-Methyl resonance frequency of $CH_3N^+(C_4H_9)_3$ salts in 1-bromonaphthalene as a function of concentration. Relatively similar curves were obtained for all the other salts studied.

Hydrogen Bonding. Coordination of Anions. A strong complexing agent which can remove anions from close proximity to cations should provide a means of decreasing the effects of ion association. Schleyer's studies have shown alcohols to be capable of hydrogen bonding to halide ions.[12] Fraenkel and Petrucci have demonstrated that slight amounts of methanol can radically change the extent of association of halide salts in low-dielectric solvents.[6,24] We find similar effects. Adding 3% methanol to a 0.04 M solution of $CH_3P^+Ph_3I^-$ in 1-bromonaphthalene shifts the α-methyl resonance of the cation upfield 38 Hz (Figure 3).

Table V. Chemical Shifts of Onium Salts in 1-Bromonaphthalene ($CH_3M^+R_3X^-$)[a]

	X^-	$-\nu$	Δ
$CH_3N^+(C_4H_9)_3$	I^-	162	36
	Pic^-	111	80
	$CH_3B^-(cyclohexyl)_3$	83	103
$CH_3P^+(C_4H_9)_3$	I^-	95	32
	Pic^-	46	74
	$CH_3B^-(cyclohexyl)_3$	19	96
$CH_3P^+Ph_3$	Cl^-	223	−20
	Br^-	204	−4
	I^-	170	24
	Pic^-	125	57
	$CH_3B^-(cyclohexyl)_3$	66	106[b]
$CH_3As^+Ph_3$	Pic^-	129	51
	$CH_3B^-(cyclohexyl)_3$	74	96[b]

[a] 0.05 M, see below for dilution effects. [b] See footnote b, Table IV.

Methanol hydrogen bonds to iodide anions and permits an enhanced cation–solvent interaction by reducing the effects of ion association. In contrast, the addition of 3% of dipolar aprotic solvents such as acetonitrile or nitrobenzene causes a much smaller upfield shift (only 5–10 Hz). It is unlikely that these solvents coordinate significantly with either cation or anion;[25] they may serve to raise the dielectric constant of the solvent, thus decreasing ion association and increasing the magnitude of the observed ASIS.

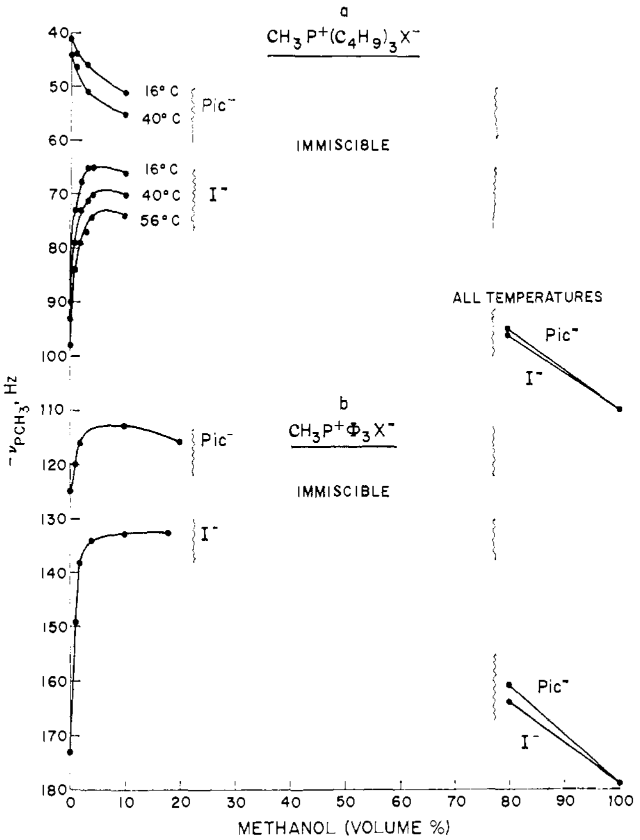

Figure 3. (a) Effect on PCH_3 resonance frequency of $CH_3P^+(C_4H_9)_3$ salts (0.04 M in 1-$C_{10}H_7Br$) of adding methanol at various temperatures. The salt concentration is held constant. (b) Effect on PCH_3 resonance frequency of $CH_3P^+Ph_3$ salts (0.04 M in 1-$C_{10}H_7Br$) of adding methanol. The salt concentration is held constant.

It is interesting to compare the effects of adding methanol to 1-bromonaphthalene solutions of some of the other salts studied (Table VI). The results are entirely consistent with the suggestion that complexation of the anion reduces effects due to ion association. Cations which are well "shielded" by anions and hence have small ASIS's experience the largest changes when methanol is added. Conversely, the downfield shifts of the α-methyl resonances of $CH_3N^+(Bu)_3Pic^-$ and $CH_3P^+(Bu)_3Pic^-$ are not surprising (Figure 3). The large upfield shifts experienced by these salts in the absence of methanol indicate anion "shielding" effects are relatively unimportant. Subsequently the dominant effect of methanol is simply to dilute the 1-bromonaphthalene, giving rise to the observed downfield shift. Similarly, the addition of methanol to 1-bromonaphthalene solutions of all the $(C_4H_9)_4B^-$ and $CH_3B^-(cyclohexyl)_3$ salts causes a downfield displacement of the cations' α-methyl resonances. It should be noted

Table VI. Effect of Methanol on Cation ASIS's[a,b]

Salt	$\Delta_{1\text{-}C_{10}H_7Br}$	Methanol effect,[c] Hz
$CH_3N^+(C_4H_9)_3Pic^-$	80	−7
$CH_3P^+(C_4H_9)_3Pic^-$	76	−5
$CH_3P^+Ph_3Pic^-$	60	11
$CH_3P^+(C_4H_9)_3I^-$	34	22
$CH_3N^+(C_4H_9)_3I^-$	36	24
$CH_3P^+Ph_3I^-$	21	38

[a] Salts are 0.04 M. [b] 3% methanol (by volume). [c] The figures represent the incremental shifts due to the addition of methanol.

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(24) G. Fraenkel and J. P. Kim, *J. Amer. Chem. Soc.*, 88, 4203 (1966).
(25) J. F. Coetzee and J. J. Campion, *ibid.*, **89**, 2517 (1967).

that even at a concentration of 20% methanol, iodide salts still experience a smaller ASIS than picrate salts, indicating that under these conditions methanol does not completely eliminate cation–anion association (Figure 3).

Addition of methanol also reduces the effects attributed to ion association in other solvents (Figure 4). Other proton donors which hydrogen bond are also capable of decreasing anion "shielding" effects. Slight quantities of ethanol, *t*-butyl alcohol, and chloroform when added to 1-bromonaphthalene solutions of $CH_3P^+Ph_3I^-$ all shifted the cation α-methyl resonance frequency further upfield.[26] Further studies of this hydrogen bonding phenomenon, complemented by an infrared investigation of the same systems, are in progress.

A logical extension of the anion solvation studies would be the selection of a solvent such as benzyl alcohol, which is both aromatic and capable of hydrogen bonding as well. In this solvent the α-methyl resonance frequencies of the $CH_3P^+Ph_3$ and $CH_3As^+Ph_3$ cations are independent of halide anion (Table VII), again indicating that the strong ion–solvent interaction drastically reduces the "shielding" capabilities of the halides. Results in methanol are also shown. The elimination of "shielding" is in no way attributable to the higher dielectric constant of benzyl alcohol compared to 1-bromonaphthalene. Similar experiments using an isodielectric constant nitrobenzene–1-bromonaphthalene mixture (~40–60, v/v, $D \approx 12$) still revealed significant anion effects (Table VII).

Table VII. Magnetic Resonance Frequencies of Various Salts in Hydrogen Bonding Solvents and Comparison with an Isodielectric Mixture[a]

	Solvent		
	CH_3OH $-\nu$	C_6H_5-CH_2OH $-\nu$	1-$C_{10}H_7Br$–$C_6H_5NO_2$ $-\nu$
$CH_3N^+(C_4H_9)_3I^-$	183	139	
Pic^-	182	130	
$CH_3P^+(C_4H_9)_3I^-$	110	75	
Pic^-	109	67	
$CH_3P^+Ph_3Cl^-$	179	130	207
Br^-	179	130	188
I^-	179	130	164
Pic^-	179	124	144
$CH_3As^+Ph_3Cl^-$	176	130	
Br^-	176	130	
I^-	176	130	
Pic^-	175	125	

[a] Salts are 0.05 *M*

Geometric Effects. Cations. The α-methyl resonance frequency of $CH_3P^+(o\text{-tolyl})_3I^-$ is shifted considerably further upfield in 1-bromonaphthalene than are the α-methyl resonances of the other methyltriarylphosphonium iodides (Table VIII). This result must be a consequence of ion association as no such effect is observed in benzyl alcohol or when inefficient "shielders" such as picrate or $CH_3B^-(cyclohexyl)_3$ are substituted in place of iodide. The relatively large ASIS of $CH_3P^+(o\text{-tolyl})_3I^-$ in 1-bromonaphthalene may be caused by destabilization of the associated species due to unfavorable interaction between the iodide anion and the nearby *ortho* methyl groups.

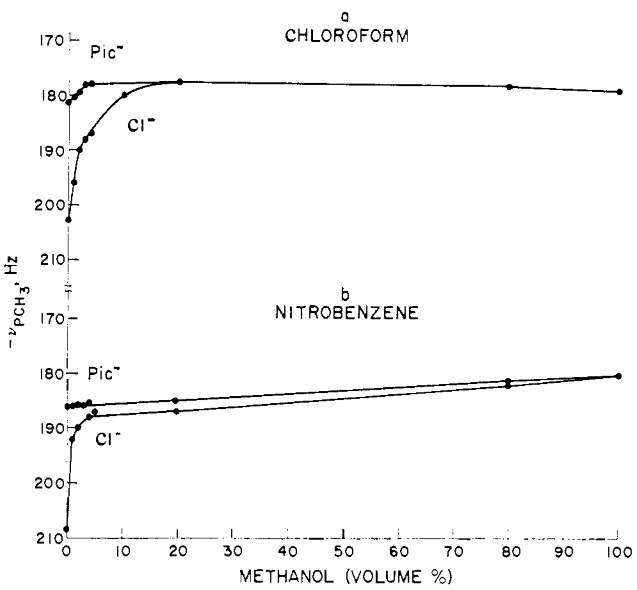

Figure 4. (a) Effect on PCH_3 resonance frequency of $CH_3P^+Ph_3$ salts (0.05 *M* in $CDCl_3$) of adding methanol. The salt concentration is held constant. (b) Effect on PCH_3 resonance frequency of $CH_3P^+Ph_3$ salts (0.05 *M* in $C_6H_5NO_2$) of adding methanol. The salt concentration is held constant.

Table VIII. Chemical Shifts of Arylphosphonium Salts ($CH_3P^+(Ar)_3X^-$)[a]

	Solvent		
Ar	$CDCl_3$ $-\nu$	1-$C_{10}H_7Br$ Δ	$C_6H_5CH_2OH$ Δ
	X^- = Iodide$^-$		
o-Tolyl	194	44	65
Phenyl	194	21	66
m-Tolyl	190	2	54
p-Tolyl	184	−3	50
	X^- = Picrate$^-$		
o-Tolyl	183	68	60
Phenyl	182	57	58
m-Tolyl	176	40	47
p-Tolyl	173	34	45
	X^- = $CH_3B^-(cyclohexyl)_3$[b]		
o-Tolyl	(173)	94	
Phenyl	(172)	107	
m-Tolyl	(166)	82	

[a] 0.05 *M*. [b] See footnote *b*, Table IV.

In distinction to the *ortho* compound, the *differences* in the ASIS's of the α-methyl resonances of the unsubstituted and *meta*- and *para*-substituted arylphosphonium salts are reasonably *independent* of anion for a given solvent (Table VIII). This indicates that cation solvation differences rather than ion association may be the determining factors for these salts.

2. Anions. The α-methyl resonance frequencies of some $CH_3B^-(Ar)_3$ and $CH_3B^-(cyclohexyl)_3$ salts are independent of the cations investigated in a variety of

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(26) As these solvents cause larger upfield shifts (~10 to 20 Hz) and are of lower dielectric constant than acetonitrile, hydrogen bonding effects must be responsible. Addition of slight quantities of low-dielectric solvents which do not hydrogen bond significantly (such as acetone or methylene chloride) caused very slight upfield shifts (~2 Hz).

Table IX. Resonance Frequencies of Anions in Various Solvents[a]

Nonaromatic Solvents

Solvent	$CH_3B^-Ph_3$[b] ν	CH_3B^-(cyclohexyl)$_3$[c] ν
$CDCl_3$	−20	52
CH_3COCH_3	−19	49
CH_2Cl_2	−15	51
CH_3NO_2	−14	56
CH_3CN	−12	56

Aromatic Solvents

Solvent	$CH_3B^-Ph_3$[d] $-\nu$	$CH_3B^-Ph_3$[d] Δ	CH_3B^-(cyclohexyl)$_3$[e] $-\nu$	CH_3B^-(cyclohexyl)$_3$[e] Δ
C_6H_5Br	49	−29	−15	−37
C_6H_5CN	55	−35	−8	−44
$C_6H_5CH_2OH$	56	−36	*f*	
$C_6H_5NO_2$	58	−38	−4	−48
1-$C_{10}H_7Br$	85	−65	23	−75

Other Anions

Salt	$CDCl_3$ $-\nu$	1-$C_{10}H_7Br$ Δ	C_6H_5-CH_2OH Δ
$CH_3P^+Ph_3CH_3B^-$(*o*-tolyl)$_3$	29	−62	−36
$As^+Ph_4CH_3B^-$(*o*-tolyl)$_3$	29	−66	−37
$As^+Ph_4CH_3B^-$(*p*-tolyl)$_3$	16	−74	−42

Ring Methyl Resonances of Tolyl Derivatives: $As^+Ph_4CH_3B^-(PhCH_3)_3$

	$CDCl_3$ $-\nu$	1-$C_{10}H_7Br$ Δ	$C_6H_5CH_2OH$ Δ
ortho	122	−59	−29
para	126	−22	−4

[a] Salts are 0.05 *M*. [b] $CH_3P^+Ph_3$ cation; same results for CH_3N^+-$(C_4H_9)_3$ cation. [c] $(CH_3)_4N^+$ cation; same results for other R_4N^+ cations, and for $CH_3P^+Ph_3$ cation and As^+Ph_4 cation. [d] $CH_3P^+Ph_3$ cation. [e] $CH_3P^+Ph_3$ cation; for other cations see Table X. [f] Decomposed.

nonaromatic solvents (Table IX).[27,28] Solvent polarity had little effect on the anions' α-methyl resonances. Aromatic solvents cause large downfield ASIS's for these anions. Downfield shifts have also been observed for uncharged polar molecules which have protons near the negative ends of the dipole.[30] Repulsion between the anion's negative site and the electron-rich part of the aromatic ring causes the anion to approach the solvent molecule in the plane of the ring. Thus, the anion's α-methyl group experiences a *downfield* shift due to the diamagnetic anisotropy of the ring.[30] With these anions both polar and nonpolar aromatic solvents cause downfield shifts, indicating that polar groups do not substantially alter the anion–solvent orientation. In contrast to this, it should be recalled that polar aromatic solvents have only a small effect on cation resonances. The methyl group of the *o*-tolyl derivative exhibits the largest ASIS of the ring methyls. Thus, as with the cations, the primary interaction site between ion and solvent molecule is at the charged central atom.

Ion Association. "Shielding" of Anions by Cations. Only in 1-bromonaphthalene and bromobenzene is the magnitude of Δ dependent upon the accompanying cation (Table X). It can be seen that in these two solvents Δ is proportional to cation size. In analogy with the interpretation previously made for the cations, we feel that close association between ions enables cations to "shield" anions from the aromatic solvent. It should be noted that the smaller cations are the more efficient "shielders." In the higher dielectric aromatic solvents "shielding" effects are substantially reduced, presumably because of a considerable decrease in the degree of ion association (Table X).

Table X. Dependence of Chemical Shift of Anion on Cation $M^+CH_3B^-$(cyclohexyl)$_3$ Salts[a]

	Solvent				
M	$CDCl_3$ ν	1-C_{10}-H_7Br Δ	C_6H_5Br Δ	C_6H_5-NO_2 Δ	C_6H_5CN Δ
$(CH_3)_4N^+$	52	−47	−23	−47	−43
$(C_2H_5)_4N^+$	52	−60	−27	−47	−43
$(C_3H_7)_4N^+$	52	*b*	−27	−47	−43
$CH_3N^+(C_4H_9)_3$	52	−60	−27	−47	−43
$CH_3P^+(C_4H_9)_3$	52	−58	−26	−47	−43
$(C_4H_9)_4N^+$	52	−60	−27	−47	−43
$CH_3P^+Ph_3$	(52)	−75[c]	−34[c]	−47[c]	−43[c]
As^+Ph_4	52	−82	−36	−47	−43

[a] 0.05 *M*, anion resonances change less than 4 Hz with 10-fold dilution. [b] Anion α-methyl resonance obscured by proton resonances of cation. [c] See Footnote *b* of Table IV.

Dipole–Cation Interaction. Coordination of Cations. In analogy to the methanol studies on cations, it would be of interest to obtain an agent capable of complexing with cations. Gilkerson's conductance experiments have demonstrated that triphenylphosphine oxide coordinates with cations.[1a] The results of adding various quantities of triphenylphosphine oxide to a solution of $(CH_3)_4N^+CH_3B^-$(cyclohexyl)$_3$ provide independent support of his work (Figure 5). The fact that both cation and anion move downfield is consistent with the formation of a cation–triphenylphosphine oxide complex. The $(CH_3)_4N^+$ cation is apparently more efficiently "shielded" by triphenylphosphine oxide than by the anion, thus explaining its decreased ASIS. At the same time, complexation of $(CH_3)_4N^+$ with triphenylphosphine oxide reduces the cation's "shielding" effects, thus increasing the downfield ASIS of the anion.[31] The excellent correlation between the α-methyl resonance frequency shifts of the $(CH_3)_4N^+$ cation and the CH_3B^--(cyclohexyl)$_3$ anion due to the addition of triphenylphosphine oxide lends further support to the proposed model (Figure 5c). As would be expected, triphenylphosphine oxide caused very small shifts of the cation and anion resonances in high-dielectric solvents such as nitrobenzene.

As another test triphenylphosphine oxide was added to 1-bromonaphthalene solutions of various CH_3B^--

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(27) The rather high-field resonances observed (note that some CH_3B^--(cyclohexyl)$_3$ resonances are *upfield* of TMS) are expected for methyl groups bonded to negatively charged metals.[13]

(28) In a previous paper,[29] we noted that ion pairing in solutions of $CH_3N^+(C_4H_9)_3B^-Ph_4$ places the cation α-methyl group in close proximity to the phenyl rings of the anion, thus giving rise to a large upfield shift of the cation α-methyl resonance frequency due to the diamagnetic anisotropy of the anion. None of the cations investigated (As^+Ph_4, $CH_3P^+(Ar_3)$, or R_4N^+) was found capable of affecting anion proton magnetic resonance frequencies in low-dielectric nonaromatic solvents. The reasons for this unusual behavior are uncertain and are currently under investigation.

(29) R. P. Taylor and I. D. Kuntz, Jr., *J. Amer. Chem. Soc.*, 91, 4006 (1969).

(30) N. S. Bhacca and D. H. Williams, *Tetrahedron Lett.*, 42, 3127 (1964).

(31) This also provides evidence that triphenylphosphine oxide does not coordinate with the anion. If it did, the magnitude of the anion's Δ would be expected to *decrease*.

Table XI. Effect of Triphenylphosphine Oxide on Anion ASIS's For Various Salts in 1-Bromonaphthalene[a,b]

Salt	Δ 1-$C_{10}H_7Br$	Triphenylphosphine oxide effect,[c] Hz
$(CH_3)_4N^+CH_3B^-$(cyclohexyl)$_3$	−46	−29
$(C_4H_9)_4N^+CH_3B^-$(cyclohexyl)$_3$	−62	−20[d]
$CH_3P^+Ph_3CH_3B^-$(cyclohexyl)$_3$	−77[e]	−7
$As^+Ph_4CH_3B^-$ (cyclohexyl)$_3$	−82	−4

[a] Salts are 0.05 *M*. [b] Triphenylphosphine oxide is 0.67 *M*. [c] The figures represent the incremental downfield shifts due to addition of $OPPh_3$. [d] ±6 Hz; uncertain due to interference of cation resonances. [e] See footnote *b*, Table IV.

(cyclohexyl)$_3$ salts (Table XI). The important result is that the smaller the cation, the larger the effect of triphenylphosphine oxide. This is completely analogous to the results obtained using methanol to complex with anions.

Geometric Effects. Anions. With the few cations studied the ASIS experienced by the anion α-methyl group of the methyltriarylboron salts is much less sensitive to ring methyl substitution (Table IX). For the large bulky cations under consideration ion association should not be significantly affected by ring methyl substitution on the anions. The fact that the trend in ASIS shifts is opposite to that observed for cations (*i.e.*, the *para*-substituted compound exhibits the largest ASIS) supports the idea that the anion–solvent geometry must be very different from the cation–solvent geometry.

Table XII. Effect of Temperature on Chemical Shifts of Salts in 1-Bromonaphthalene[a]

Salt	$-\nu_{40°}$	$-\nu_{135°}$	$\Delta_{40°}$	$-(\nu_{135°} - \nu_{40°})$
Cation Resonances				
$CH_3P^+Ph_3I^-$	170	179	24	9
$CH_3N^+(C_4H_9)_3I^-$	162	169	36	7
$CH_3P^+Ph_3Pic^-$	122	131	60	9
$CH_3N^+(C_4H_9)_3Pic^-$	112	127	79	15
$CH_3N^+(C_4H_9)_3CH_3B^-$(cyclohexyl)$_3$	85	115	101	30
$CH_3P^+Ph_3CH_3B^-$(cyclohexyl)$_3$	65	101	106[b]	36
$(CH_3)_4N^+CH_3B^-$(cyclohexyl)$_3$	57	90	143	33
Anion Resonances				
$(CH_3)_4N^+CH_3B^-$(cyclohexyl)$_3$	−5	−11	−47	−6
$CH_3N^+(C_4H_9)_3CH_3B^-$(cyclohexyl)$_3$	8	0	−60	−8
$CH_3P^+Ph_3CH_3B^-$(cyclohexyl)$_3$	26	10	−77[b]	−16
$As^+Ph_4CH_3B^-$(cyclohexyl)$_3$	32	15	−83	−17

[a] Salts are 0.05 *M*. [b] See footnote *b*, Table IV.

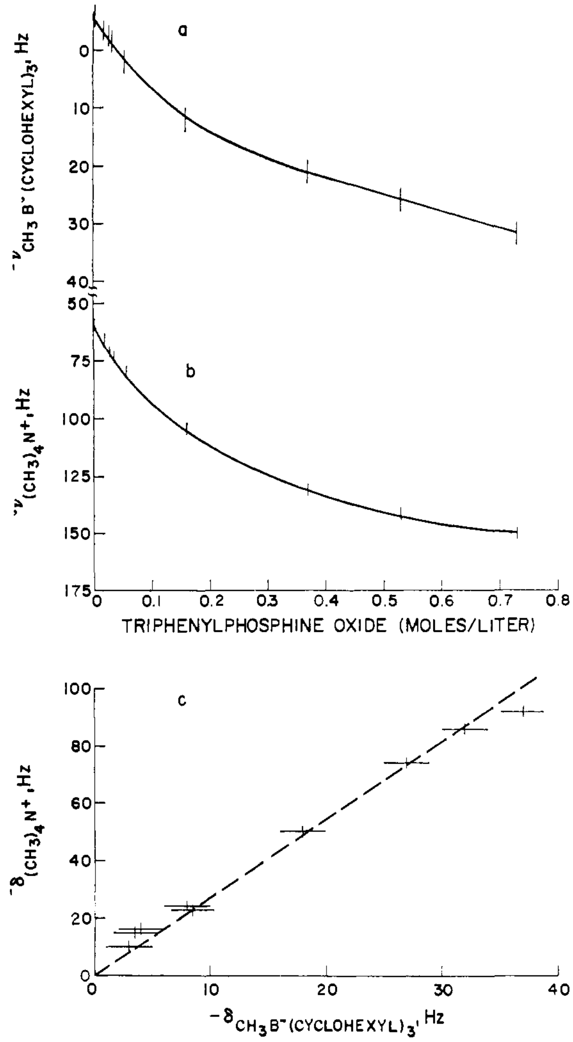

Figure 5. (a) Effect on BCH_3 resonance of $(CH_3)_4N^+CH_3B^-$(cyclohexyl)$_3$ (0.05 *M* in 1-$C_{10}H_7Br$) on adding triphenylphosphine oxide. (b) Effect on $(CH_3)_4N^+$ resonance of $(CH_3)_4N^+CH_3B^-$(cyclohexyl)$_3$ (0.05 *M* in 1-$C_{10}H_7Br$) on adding triphenylphosphine oxide (note scale change). (c) Triphenylphosphine oxide effect on $(CH_3)_4N^+$ resonance *vs.* triphenylphosphine oxide effect on BCH_3 resonance. δ is the incremental downfield shift due to addition of triphenylphosphine oxide.

3. Temperature Effects. Variable temperature studies on representative systems were performed in an effort to assess the relative enthalpies of the various interactions which have been discussed. The magnitudes of the ASIS's of polar solute molecules decrease at higher temperatures ($-\Delta H \sim$ 1–2 kcal)[32,33] and it is likely that this is true for ionic solutes as well. It is believed that elevated temperature favors ion association, but there is some question regarding this point of view.[29] Hydrogen bonding ($-\Delta H \sim$ 3–6 kcal)[12,34] and ion–dipole interactions[35] should be characterized by negative enthalpies and would be expected to decrease as the temperature is raised.

The magnitudes of ASIS effects for various cations and anions decrease at higher temperatures (Table XII). In general, ions which exhibit the largest Δ's at lower temperatures experience the greatest decrease in Δ when the temperature is raised.[36] Unfortunately, this observation can be explained in terms of either the formation of more association species or the reduction of ion–aromatic solvent interactions.

The effect of methanol at various temperatures in 1-bromonaphthalene solutions of some $CH_3P^+(C_4H_9)_3$ salts was determined (Figure 3a). The methanol effects are largest at the lowest temperature studied, consistent with the fact that the methanol–iodide interaction must be characterized by a negative enthalpy. Examination of the triphenylphosphine oxide–cation

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(32) M. D. Johnston, Jr., F. P. Gasparro, and I. D. Kuntz, *J. Amer. Chem. Soc.*, **91**, 5715 (1969).

(33) I. D. Kuntz and M. D. Johnston, *ibid.*, **89**, 6008 (1967).

(34) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960, p 82.

(35) R. H. Stokes, *J. Amer. Chem. Soc.*, **86**, 979 (1964).

(36) Plots of ln Δ *vs.* $1/T$ suggest an approximate ΔH for all these systems of magnitude ~1 kcal/mol.

interaction, which also should have a negative enthalpy, yields a similar result.

Discussion

A wide range of aromatic solvents are capable of producing sizable ASIS shifts for the cations and anions of this study. The magnitude of these effects often depends upon the size and shape of the ions as well as the nature of the solvent. The most striking observation is that small ions are more efficient "shielders" than larger ones.

We believe the results may be explained on the basis of the following model. We assume that in low-dielectric solvents ($D < 15$) all of the salts studied are highly associated in the nmr concentration range; two classes of associated species may be envisioned, contact and solvent separated. Contact species will be characterized by relatively short interionic distances with no intervening solvent molecules between the charge sites; solvent-separated species will have longer interionic distances due to the presence of one or more solvent molecules between the charge sites.[37] Such a picture suggests that the chemical shifts of the contact species are very sensitive to counterion, but that the chemical shifts of solvent-separated species are relatively independent of counterion and are dominated by solvent effects. Due to rapid exchange between these species the nmr experiment should measure a weighted average of their contributions to the observed chemical shifts. The "shielding" capabilities of ions can then be interpreted in terms of the relative number of contact and solvent-separated species which they form. We shall now consider this model in some detail.

Using the "sphere-in-continuum" model of ion association,[38] we can estimate ion *pairing* association constants of $CH_3N^+(C_4H_9)_3I^-$ and $CH_3N^+(C_4H_9)_3Pic^-$ at a dielectric constant of 4.7 (dielectric constant of 1-bromonaphthalene at 40°) by extrapolation of the results of conductance studies.[39] It is also possible to make estimates using the ion size parameters obtained in these studies. The association constants obtained from the two methods are in good agreement (Table XIII). It is clear that this model, which allows only for contact ion pairs, predicts that at all the concentrations we investigated the salts are 100% associated. We note that the "sphere-in-continuum" model alone is not sufficient to explain the large "shielding" differences observed for the picrate and iodide anions in the concentration range investigated (Figure 2).

Table XIII. Estimation of Ion Pairing Association Constants for Methyltributylammonium Salts

Salt	K,[a] l./mol	K,[b] l./mol
$CH_3N^+(C_4H_9)_3Pic^-$	6×10^8	1.0×10^8
$CH_3N^+(C_4H_9)_3I^-$	8×10^8	1.1×10^9

[a] Figures were obtained by extrapolation of data on corresponding tetrabutylammonium salt[c] in nitrobenzene–carbon tetrachloride mixtures.[39] [b] Calculations were made using ion size parameters which were determined in the same experiment. [c] The systems are sufficiently similar that a *comparison* of the constants of the iodide and picrate salts should be meaningful.

If we accept the association constants estimated from conductivity we conclude that there are differences in the nature of the associated species for the picrate and iodide salts; the small iodide anion, being a better "shielder," must form more contact species than the larger picrate anion. Similar calculations indicate the other salts we studied are also 100% associated in 1-bromonaphthalene. In order to explain the trends in "shielding," we postulate that when ion association occurs in noncoordinating solvents such as 1-bromonaphthalene large bulky cations and anions form mostly solvent-separated species, whereas smaller ions favor formation of contact species.

For the sake of argument, we consider other explanations. One can assume that a given cation forms only contact species with a variety of anions, and the reason it experiences an anion dependent solvent shift is due to variation in the solvent–anion interaction.[21] We believe such assumptions are incompatible with our experimental observations. Cations of tetraalkylboron salts experience solvent shifts of such magnitude that there must be on the average very close approach between cations and solvent molecules;[40] hence most of the associated species are solvent separated.

On the other hand, the extremely small (or even negative) Δ's of ammonium and phosphonium cations in the presence of halide anions is indicative of a substantial change in the cation–solvent interaction. If it is assumed that halide ions, like the tetraalkylboron anions, form mostly solvent-separated species, but reduce Δ by changing the orientation between the cations and aromatic solvent, it would be necessary to postulate an anion–solvent interaction of considerable strength. This explanation is unlikely, considering that for the strongest solvent–anion interaction we have found (benzyl alcohol–halide ions) the cation chemical shift was independent of halide anion. It is more reasonable to assume that in 1-bromonaphthalene a greater percentage of the associated species are contact for the smaller halide ions.

We are thus led to the following conclusion. In low-dielectric aromatic solvents where ion association is expected, the "shielding" abilities of an ion are commensurate with its potential to form contact species; those ions which form the most contact species will be the best "shielders," and those ions which give rise to mostly solvent separated species will be the least effective "shielders." Though we cannot delineate the relative populations and stoichiometries of the various associated species in solution, the nmr evidence indicates that in low-dielectric solvents small ions in general form more contact species than larger ones.[41]

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(37) For similar views, see E. Grunwald, *Anal. Chem.*, **26**, 1696 (1954).

(38) A. D'Aprano and R. M. Fuoss, *J. Phys. Chem.*, **67**, 1871 (1963).

(39) E. Hirsch and R. M. Fuoss, *J. Amer. Chem. Soc.*, **82**, 1018 (1960).

(40) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(41) The differences in Δ between alkyl and aryl phosphonium salts deserve special consideration (Table XIV). When the accompanying anion is an efficient "shielder" (such as iodide) the $CH_3P^+Ph_3$ ion has the smaller ASIS in 1-bromonaphthalene, indicating it forms *more* contact species with the small iodide anion than does the corresponding $CH_3P^+(C_4H_9)_3$ cation. The results are reverse in benzyl alcohol. In this solvent the $CH_3P^+Ph_3$ cation experiences the larger ASIS. Similarly, when the accompanying anion is CH_3B^-(cyclohexyl)$_3$, the $CH_3P^+Ph_3$ cation also exhibits a larger ASIS in 1-bromonaphthalene than does the $CH_3P^+(C_4H_9)_3$ cation. This indicates the $CH_3P^+(C_4H_9)_3$ cation forms more contact species with large anions than does the $CH_3P^+Ph_3$ cation. This interpretation is supported by the observation that the $CH_3P^+(C_4H_9)_3$ ion "shields" CH_3B^-(cyclohexyl)$_3$ more effectively than does the $CH_3P^+Ph_3$ cation (Table X). Our results indicate the *nature* of the associated species for alkyl- and arylphosphonium salts is very dependent upon counterion. Aryl salts form more contact species with small

Table XIV. Chemical Shifts of Alkyl- and Arylphosphonium Salts ($CH_3P^+Ph_3X^-$ and $CH_3P^+(C_4H_9)_3X^-$)[a]

	Solvent		
Salt	$CDCl_3$ $-\nu$	1-C_{10}-H_7Br Δ	C_6H_5-CH_2OH Δ
$CH_3P^+Ph_3I^-$	194	24	64
$CH_3P^+(C_4H_9)_3I^-$	127	32	52
$CH_3P^+Ph_3CH_3B^-$(cyclohexyl)$_3$	(172)[b]	106[b]	*c*
$CH_3P^+(C_4H_9)_3CH_3B^-$(cyclohexyl)$_3$	115	96	*c*

[a] Salts are 0.05 *M*. [b] See footnote *b*, Table IV. [c] Decomposed.

We can think of two possible reasons why large cations and anions form fewer contact species in the low-dielectric solvents investigated; first unfavorable steric interactions between the bulky substituents of these ions may prevent close approach of the charge sites. These effects can be nonspecific or the steric hindrance can be localized. An example of the latter effect is the unusually large ASIS of $CH_3P^+(o\text{-tolyl})_3I^-$ in 1-bromonaphthalene, suggesting that this salt forms relatively fewer contact species than $CH_3P^+Ph_3I^-$ in this solvent.

A second possibility is that the larger ions are more solvated than small ions in low-dielectric solvents, an effect presumably due to van der Waals interactions between the polarizable groups of the ions and solvent.[44] These interactions facilitate the solution of salts of large ions into low-dielectric solvents in which salts of small ions are insoluble. Such ion–solvent interactions are clearly more important for larger ions and would be expected to stabilize the solvent-separated species over the contact forms.

It would be of interest to reconsider the results obtained in nonaromatic solvents. In principle it should be possible to obtain the same information concerning ion association as obtained from nmr studies in low-dielectric aromatic solvents. Reinspection of Tables IV and V reveals that those anions which are considered to be the most effective "shielders" (*i.e.*, form the most contact species) also cause the greatest downfield shifts of cations' α-methyl resonances in both polar aromatic and nonaromatic solvents. Though the results in these solvents depend upon both the extent of association and the electric field generated by a given anion, it is interesting to note that the relative ordering of the anions with respect to these effects in chloroform parallels their relative "shielding" order in low-dielectric aromatic solvents (Figure 6).

The cations we have investigated do not shift the α-methyl resonance frequency of $CH_3B^-Ph_3$ or CH_3B^-(cyclohexyl)$_3$ in nonaromatic solvents. Though it is probable that extensive ion association occurs in low-dielectric solvents such as chloroform, it should be noted that the range of cations studied is much more restricted than for anions. In each case the positive charge is "buried" under sizable organic substituents. Apparently these large cations do not appreciably distort the anion charge density;[45] and in addition it is likely they form mostly solvent-separated species.

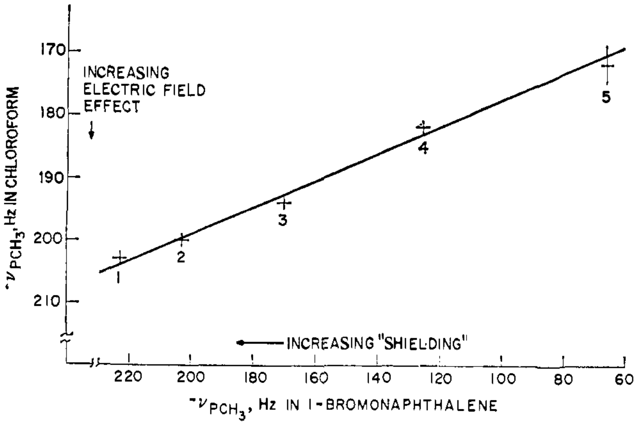

Figure 6. Chemical shifts of $CH_3P^+Ph_3X^-$ (0.05 *M*) salts in 1-bromonaphthalene and chloroform-*d*: (1) $X^- = Cl^-$, (2) $X^- = Br^-$, (3) $X^- = I^-$, (4) $X^- = Pic^-$, (5) $X^- = CH_3B^-$(cyclohexyl)$_3$ (see footnote *b*, Table IV).

The fact that the α-methyl resonance frequencies of the various cations studied are *insensitive* to anion in methanol is consistent with our previous discussion concerning hydrogen bonding. As effects due to ion association are greatly reduced in methanol, this solvent might also have served as the reference solvent. Chloroform was chosen instead because it was hoped that electric field effects in this solvent and 1-bromonaphthalene would be approximately equal, and thus cancel out, leaving only "shielding" effects. Because of the relatively small field effects the discussion is unaltered if methanol is chosen as the reference solvent instead.

Solvation and Coordination.[46] Though all dissolved solute molecules are solvated in that they are surrounded by solvent molecules, there are definitely differences in the relative strengths and specificities of the various possible ion–solvent interactions. Aromatic solvents help us to define the nature of these interactions, but we would expect the results to be generally applicable to nonaromatic solvents as well.

Nonpolar solutes dissolve in aromatic solvents with small ASIS effects;[15] the dispersion interactions which bring nonpolar molecules into solution are sufficiently isotropic, so that the average solute–solvent geometry is not much different from the TMS–solvent geometry. These dispersion forces also allow ions to dissolve in low-dielectric aromatic solvents, but in addition it is clear that the ionic charges cause the solvent to assume a much different average orientation with respect to these molecules than is postulated for nonpolar solute molecules. Whereas both TMS and ionic solutes are solvated in aprotic aromatic solvents, we think of the ion–solvent interaction as much more directional, though it is doubtful that an ion–solvent complex of fixed stoichiometry exists as a stable kinetic entity in solution.

Even very polar solvents such as nitrobenzene or nitromethane do not appear to interact significantly

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anions, and alkyl salts form more contact species with large anions. Despite the large number of conductance experiments which have been performed on tetraalkylammonium salts,[42] few tetraalkyl- or tetraarylphosphonium salts have been studied.[43] Clearly, conductometric investigations of such salts in a wide range of solvents and with a variety of anions would be of interest.

(42) See for example, D. S. Berns and R. M. Fuoss, *J. Amer. Chem. Soc.*, **82**, 5585 (1960).

(43) C. A. Kraus, *J. Phys. Chem.*, 60, 129 (1956).

(44) E. Grunwald and E. Price, *J. Amer. Chem. Soc.*, **86**, 4517 (1964).

(45) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, New York, N. Y., 1962, p 157.

(46) For similar views, see M. Szwarc, "Carbanions, Living Polymers, and Electron Transfer Processes," Interscience, New York, N. Y., 1968, p 287.

Table XV. Analytical Data[a]

Compound	Mp, °C	% carbon		% hydrogen		% nitrogen	
		Calcd	Found	Calcd	Found	Calcd	Found
$(CH_3)_4N^+$-CH_3B^-(cyclohexyl)$_3$	163–165	79.05	78.84	13.85	13.86	4.01	3.93
$CH_3N^+(C_2H_5)_3$-$B^-(C_4H_9)_4$	99–101	77.71	77.51	15.31	14.89	3.94	4.57
$(C_2H_5)_4N^+$-CH_3B^-(cyclohexyl)$_3$	110–112	79.96	79.78	13.92	14.02	3.45	3.42
$CH_3N^+C_7H_{13}$-$B^-(C_4H_9)_4$	120–123	78.87	78.55	14.34	13.88	3.38	3.86
$CH_3N^+(C_3H_7)_3Pic^-$	78–81	49.73	49.56	6.78	7.01	14.50	14.31
$(C_3H_7)_4N^+$-CH_3B^-(cyclohexyl)$_3$	132–134	80.65	80.46	13.97	14.16	3.03	3.03
$CH_3N^+(C_4H_9)_3Pic^-$	42–44[b]	53.26	53.01	7.53	7.75	13.08	12.95
$CH_3N^+(C_4H_9)_3$-$CH_3B^-Ph_3$	101–103	84.00	83.97	10.57	10.53	3.06	2.84
$CH_3N^+(C_4H_9)_3$-B^-Ph_4	162–163	85.52	85.43	9.70	9.90	2.70	2.56
$CH_3N^+(C_4H_9)_3$-CH_3B^-(cyclohexyl)$_3$	124–126	80.80	80.32	13.99	14.18	2.94	2.95
$(C_4H_9)_4N^+$-CH_3B^-(cyclohexyl)$_3$	116–118	81.19	80.89	14.02	14.23	2.71	2.69
$CH_3N^+(C_5H_{11})_3Pic^-$	52–54	56.39	56.15	7.74	7.99	11.96	11.79
$CH_3N^+(C_6H_{13})_3Pic^-$	37–39	58.57	58.82	8.65	8.47	10.92	10.80
$CH_3P^+(C_4H_9)_3I^-$	143–146[c]	45.35	45.87	8.78	8.38		
$CH_3P^+(C_4H_9)_3Pic^-$	50–52	51.23	51.22	7.24	7.14	9.47	9.47
$CH_3P^+(C_4H_9)_3$-CH_3B^-(cyclohexyl)$_3$	114–116	78.01	77.89	13.50	13.62		
$CH_3P^+Ph_3$-$CH_3B^-Ph_3$	173–174	85.55	85.71	6.75	7.02		
$CH_3P^+Ph_3$-CH_3B^-(*o*-tolyl)$_3$	183–185	85.40	85.67	7.34	7.57		
$CH_3P^+Ph_3$-CH_3B^-(cyclohexyl)$_3$	114–117	82.59	82.37	9.85	9.79		
CH_3P^+(*o*-tolyl)$_3I^-$	205–207[d]	59.20	58.99	5.42	5.26		
CH_3P^+(*o*-tolyl)$_3$-CH_3B^-(cyclohexyl)$_3$	105–107	82.80	82.39	10.17	9.96		
CH_3P^+(*m*-tolyl)$_3Pic^-$	84–85.5	61.44	61.68	4.99	5.00	7.49	7.63
CH_3P^+(*m*-tolyl)$_3$-CH_3B^-(cyclohexyl)$_3$	106–108	82.80	82.39	10.17	9.99		
$CH_3As^+Ph_3$-CH_3B^-(cyclohexyl)$_3$	83–85	76.51	76.19	9.12	8.88		
$As^+Ph_4CH_3B^-$(*o*-tolyl)$_3$	191–193	80.94	80.92	6.49	6.56		
$As^+Ph_4CH_3B^-$(*p*-tolyl)$_3$	162–164	80.94	80.79	6.49	6.61		
$As^+Ph_4CH_3B^-$(cyclohexyl)$_3$	132–134	78.41	78.26	8.57	8.86		

[a] Analyses were performed by Baron Consulting Co., Orange, Conn. 06477. [b] Mp 28°: L. F. Gleysteen and C. A. Kraus, *J. Amer. Chem. Soc.*, **69**, 452 (1947). [c] Mp 134°: W. C. Davis and W. J. Jones, *J. Chem. Soc.*, **132**, 33 (1929). [d] Mp 234°: G. B. Deacon and R. A Jones, *Aust. J. Chem.*, **16**, 499 (1963).

more strongly with ions than do the low-dielectric solvents. There is much evidence that there are considerably stronger ion–solvent interactions such as ion–dipole (*e.g.*, $(CH_3)_4N^+$–$OPPh_3$) and hydrogen bonding (*e.g.*, I^-–CH_3OH). These interactions are characterized by the coordination of a discrete number of solvent molecules to the ion in question.[47] Presumably, these interactions are sufficiently strong and directional in nature that an ion–solvent complex of fixed composition is formed. The ASIS results clearly demonstrate that specific interactions (such as hydrogen bonding) can be more important than solvent dielectric constant in determining the properties of an ionic solution.[48]

We can make rough estimates of the relative magnitudes of the various interactions under consideration. In the concentration ranges investigated in 1-bromonaphthalene, $CH_3N^+(C_4H_9)_3$ salts probably undergo a higher order equilibrium, perhaps between ion pairs and quadrupoles. Using the concentration dependence of the solvent shifts we estimate the association constants for such equilibria as of order 100 l./mol and 50 l./mol for the iodide and picrate salts, respectively. Assuming the triphenylphosphine oxide–$(CH_3)_4N^+$ equilibrium involves the formation of a 1:1 complex, it has an equilibrium constant of about 10 in 1-bromonaphthalene. Similar assumptions regarding the iodide–methanol equilibrium yield an equilibrium constant of about 10.

The trends observed in both aromatic and nonaromatic solvents are sufficiently similar that we are led to the following conclusions: the interactions which govern ion association in low-dielectric solvents are relatively weak; ion–dipole and hydrogen bonding interactions can significantly affect the state of associa-

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tion. Though the dielectric constant of the solvent influences the extent of association of a given salt, it is clear that ion size and solvent coordinating ability are important factors which can determine the *nature* of the associated species in solution.

Appendix

Elemental analysis was used to verify the identities of new compounds as well as those of compounds whose melting points disagreed with literature values. These data are presented in Table XV.

Nuclear Magnetic Resonance Studies of Mercury(II) Interaction with Nucleosides in Dimethyl Sulfoxide[1]

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Abstract: By using a nuclear magnetic resonance method, the formation constants of the 1:1 mercury(II) complexes with cytidine, adenosine, and guanosine in dimethyl sulfoxide at 36° were found to be 33.9, 7.2, and 5.9 l./mol, respectively. In dimethyl sulfoxide solutions containing 0.1 *M* cytidine and $HgCl_2$ concentration above 0.2 *M*, two peaks were observed for the amino group, indicating nonequivalence of the amino protons due to insufficiently fast rotation of the amino group. The mercuration leads to hindered rotation about the 4-C–N bond in cytidine. As the $HgCl_2$ concentration is decreased, the lines broaden, and coalesce into one broad peak at 0.1 *M* $HgCl_2$. As the concentration of $HgCl_2$ decreases below this value, the single peak sharpens, indicating fast rotation of the amino group. Starting with a dimethyl sulfoxide solution containing 0.1 *M* cytidine and 1 *M* $HgCl_2$, with increasing temperature the lines broaden and then also coalesce to a single peak. Mercury does not bind uridine, and forms a weaker complex with purine than with guanosine. Unlike zinc, mercury(II) does not form ternary complexes.

In 1952, Katz[2] added mercuric chloride to sodium thymonucleate (DNA) and discovered a remarkable decrease in the viscosity, as well as changes in other properties, indicating some kind of configurational rearrangement. Upon addition of excess chloride or cyanide ions, which strongly complex mercury(II), the solution regains its original viscosity. This discovery of the interaction of mercury(II) with DNA was followed by a demonstration of Thomas[3] that the mercury is bonded to the bases and led to further studies on interaction of mercury with the nucleosides.[4–7] Thomas has suggested that since the original size and shape of the DNA molecule is restored after the mercuric chloride is removed, a sufficient number of hydrogen bonds must remain in contact in the presence of mercuric chloride to provide a "skeleton" to guide the re-formation of the molecule when the reaction is reversed.

This work was motivated by the thought that useful information on the nature of interaction of mercury with nucleic acids can be obtained by a nuclear magnetic resonance (nmr) study of mercury(II) complexes of the nucleosides and purine. Dimethyl sulfoxide was used as solvent, as has been done in three previous papers from this laboratory,[8–10] because it provides adequate solubility without proton transfer, whereas the use of water as solvent causes complications in that the bond-forming hydrogens exchange rapidly with water protons. Although dimethyl sulfoxide is a hydrogen acceptor, we can take as reference state the one in which nucleoside is hydrogen-bonded to the solvent *via* the protons attached to nucleoside nitrogens, and look for further shifts of the NH, NH_2, and CH proton signals as an increasing amount of $HgCl_2$ is added.

Experimental Section

Materials. Purine and the nucleosides were obtained from Sigma Chemical Co. Anhydrous mercuric chloride was reagent grade. Dimethyl sulfoxide was purified by vacuum distillation after drying over potassium amide.

Nmr Measurements. Spectra were obtained with a Varian A-60 or a Perkin-Elmer R-20 spectrometer operated at 60 MHz. The latter instrument was operated at 36 ± 1°. With the A-60 spectrometer, a V-6031 variable temperature probe was used, and the V-6040 variable temperature controller was calibrated to ±1° by using the known chemical shifts of the CH_2 and OH proton resonances in ethylene glycol and the temperature calibration chart of Van Geet.[11] Sample preparation and the technique of chemical shift measurements were the same as described previously.[8–10] Frequencies of sharp peaks were accurate to ±0.2 Hz.

Results

(A) $HgCl_2$–Nucleoside Complexes in Dimethyl Sulfoxide (DMSO). In Figure 1 are reproduced the low-field portions of the nmr spectra of cytidine (0.1 *M*) in the absence and presence of 0.5 *M* $HgCl_2$. Plots of frequency and line width of the cytidine (C)–NH_2 signal in DMSO solution containing 0.1 *M* cytidine and

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