NMR Spectroscopic Evidence for the Structure of Iminium Ion Pairs

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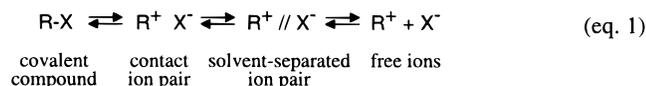
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Abstract: The NMR spectroscopic investigation of solutions of the iminium ions $Me_2N^+=C(H)Cl$ (1^+), $Me_2N^+=C(H)Ph$ ($2a^+$), and $Et_2N^+=CH_2$ (3^+) in aprotic solvents shows that the replacement of the weakly nucleophilic counterions $SbCl_6^-$, $AlCl_4^-$, BF_4^-, or $CF_3SO_3^-$ by halide ions (I^-, Br^-, Cl^-) causes a deshielding of the proton at the iminium carbon atom ($\Delta\delta_{max} = +2.8$ for $2a^+$ in CD_2Cl_2) while the chemical shifts of all other ^1H and ^{13}C nuclei remain almost unaffected. The solvent dependence of these effects, ^{14}N NMR investigations, and ab initio MO calculations suggest that iminium halides form $CH\cdots Y^-$ hydrogen bonds (Y = Cl, Br, and I) and thus exist as contact ion pairs in acetonitrile, chloroform, dichloromethane, and dimethyl sulfoxide solutions. In liquid sulfur dioxide, specific anion−cation interactions cannot be observed due to the superior solvation of the anions by SO_2.

Introduction

The importance of ion pairing in carbocation chemistry has been well recognized since Winstein's pioneering studies of solvolysis reactions[1] and has led to the dissociation scheme depicted in eq 1.

$$R\text{-}X \rightleftharpoons R^+ \; X^- \rightleftharpoons R^+ /\!/ X^- \rightleftharpoons R^+ + X^- \qquad \text{(eq. 1)}$$

covalent   contact   solvent-separated   free ions
compound   ion pair   ion pair

In contrast to the situation in the chemistry of carbanions,[2] in carbocation solutions, solvent-separated ion pairs and free ions usually cannot be distinguished by spectroscopic methods, and even the detection of contact ion pairs is difficult as long as the cation−anion interactions are only of electrostatic nature and not site-selective.[2b,3] This situation changes significantly, however, when cation, anion, and/or solvent are able to interact with each other specifically.

It has long been recognized that counterions play a significant role in the chemistry of Vilsmeier ions (chloromethyleneammonium ions). At ambient temperature only one CH_3 signal is detected in the ^1H and in the ^{13}C NMR spectra of the Vilsmeier salts **1**-Y [$Y^- = Cl^-$, $PO_2Cl_2^-$, $N(POCl_2)_2^-$][4] although the two methyl groups do not occupy equivalent positions.

Equilibria of ionic and covalent species (eq 2) have been suggested to explain this observation,[5] and the influence of

different counterions on the chemical shift of the C_{sp^2}-H was rationalized in the same way: The salt **1**-Cl shows a resonance at δ 11.11 in $CDCl_3$,[4a] whereas **1**-PO_2Cl_2—generated by the reaction of dimethylformamide with $POCl_3$—gives a signal at δ 10.05 in CH_2Cl_2.[4b] The corresponding imidophosphoryl tetrachloride [$N(POCl_2)_2^-$] of 1^+ finally resonates at δ 9.87 in $CDCl_3$.[4c]

$$\text{(eq. 2)}$$
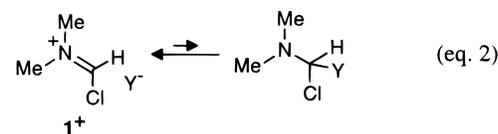
In addition, **1**-Cl and the Vilsmeier reagent obtained from dimethylformamide and $POCl_3$ were observed to show different reactivities in formylations of thiophenes.[6] It was not clear, however, whether this was due to the presence of the dichlorophosphate $1a^+$ (eq 3) or whether the electrophilicity of the (chloromethylene)dimethylammonium ion 1^+ was altered by the nature of the anion Y^- ($PO_2Cl_2^-$ vs Cl^-).[6a,7]

$$\text{(eq. 3)}$$
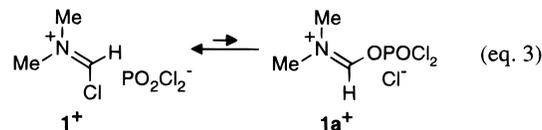
The influence of solvents on the chemical shifts of the $^+N=CH_2$ protons of methyleneammonium salts has first been

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⊗ Abstract published in *Advance ACS Abstracts,* December 1, 1997.

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Table 1. ^1H (300 MHz) and ^{13}C (75.5 MHz) NMR Chemical Shifts of Vilsmeier Salts **1**-Y in CD_3CN

	$\delta(^1H)$		$\delta(^{13}C)$	
salt	$^+N{=}CH(Cl)$	NMe	$^+N{=}CH(Cl)$	NMe
1-Cl	11.08	3.74	166.7	46.5
1-OTf	9.10	3.78/3.61	166.1	50.0/44.3
1-SbCl$_6$	8.98	3.75/3.61	165.7	50.0/44.3
1-AlCl$_4$	8.98	3.75/3.61	165.7	50.0/44.3

reported by Volz and Kiltz.[8] It was shown that the methylene resonances of the *N*-methyl-*N*-mesitylmethyleneammonium perchlorate albeit depending on the employed solvents did not correlate with their dielectric constants. As a consequence, it was stated that the observed variations of the chemical shifts were partially due to "specific orientations of solvents and solutes".[8]

Schroth et al.[9] recently reported that the $^+N{=}CHPh$ proton of (*S*)-(*E*)-1-benzylidene-2-(methoxymethyl)pyrrolidinium chloride resonates at δ 10.32 in CDCl$_3$ while the corresponding triflate gives a signal at δ 9.08 under the same conditions. An interpretation for this observation was not presented.

Despite the fact that NMR spectroscopy proved to be the most powerful tool for the structural investigation of carbocations in solutions,[10] a systematic study of the influence of the counterion on the NMR spectra of iminium salts has not yet been performed.[11] Since selective cation−anion interactions are relevant for our kinetic studies of the reactions of carbocations with nucleophiles, we set out to investigate these interactions experimentally and computationally.

In this paper we report on the first NMR spectroscopic evidence for ion pairing of iminium ions. A model for the structure of the ion pairs is presented, and the spectroscopic observations are compared with the results of ab initio MO calculations.

Results and Discussion

Proton and Carbon-13 NMR. Expecting equilibria between ionic and covalent species (eq 2), we were surprised to find the methine H of **1**-Cl (δ 11.08, in CD$_3$CN) to be 2.1 ppm more deshielded than in **1**-AlCl$_4$ (Table 1), since the percentage of covalent material should be larger in the Vilsmeier chloride **1**-Cl. Moreover, the detection of two separated, nonbroadened methyl signals in the ^1H and ^{13}C NMR spectra of **1**-OTf, **1**-AlCl$_4$, and **1**-SbCl$_6$ indicated the absence of fast exchange reactions, and the almost constant ^{13}C NMR chemical shifts of the cationic moiety also argued against the presence of variable concentrations of covalent material (Table 1).

Similar phenomena were observed in the NMR spectra of benzylideneammonium ions. As shown in Table 2, counterion effects in the NMR spectra of the *N,N*-dimethylbenzylideneammonium ions (**2a**$^+$) and *N,N*-dimethyl(*p*-methoxybenzylidene)ammonium ions (**2b**$^+$) are of comparable magnitude as those observed for Schroth's structurally analogous pyrrolidinium salts.[9] With weakly basic counterions (OTf$^-$, BF$_4^-$, SbCl$_6^-$, and AlCl$_4^-$), the chemical shifts of the $^+N{=}CHPh$ protons of **2a**$^+$ are found to be practically independent of the anion

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Table 2. Selected ^1H (300 MHz) and ^{13}C (75.5 MHz) NMR Chemical Shifts of *N,N*-Dimethylbenzylideneammonium Salts **2a**-Y and of *N,N*-Dimethyl(*p*-methoxybenzylidene)ammonium Salts **2b**-Y in CD_3CN

|	$\delta(^1H)$		$\delta(^{13}C)$	
salt	$^+N{=}CH(Ar)^a$	(E/Z)-NMe^b	$^+N{=}CH(Ar)$	NMe
2a-Cl	10.25	3.93/3.72	173.9	51.3/44.4
2a-Br	9.94	3.91/3.70	173.1	51.4/44.6
2a-I	9.53	3.85/3.67	172.5	51.7/44.8
2a-OTf	8.91	3.80/3.69	173.3	52.1/44.5
2a-BF$_4$	8.87	3.80/3.70	173.3	52.2/44.4
2a-SbCl$_6$	8.84	3.83/3.73	172.9	52.3/44.5
2a-AlCl$_4$	8.83	3.79/3.70	173.3	52.2/44.6
2b-Cl	10.05	3.79/3.70	173.3	52.2/44.6
2b-OTf	8.64	3.83/3.73	172.9	52.3/44.5

^{a} Broad singlet. ^{b} Each NMe signal is split into a doublet by spin−spin coupling with the iminium proton ($J \leq 1$ Hz). For results of NOE experiments see ref 12.

Table 3. ^1H (300 MHz) and ^{13}C (75.5 MHz) NMR Chemical Shifts of the $^+N{=}CH_2$ Fragment in Dialkylmethyleneammonium Salts R$_2$N$^+{=}$CH$_2$Y$^-$ in CD_3CN

R	salt	δ (^1H)	δ (^{13}C)	$J_{N,C}$ (Hz)^a
Et	**3**-Cl	8.40	164.1	11.8
Et	**3**-Br	8.25	162.8	—^{b}
Et	**3**-I	8.10	161.2	—^{b}
Et	**3**-OTf	7.95	166.5	12.5
Et	**3**-SbCl$_6$	7.88	166.1	12.8
Me	**4**-OTf	7.86	169.7	13.2
Me	**4**-SbCl$_6$	7.80	169.5	13.2
Me	**4**-AlCl$_4$	7.80	169.3	12.9
Pr	**5**-SbCl$_6$	7.87	167.8	12.5
*i*Pr	**6**-SbCl$_6$	8.05	163.5	12.3
Bu	**7**-SbCl$_6$	7.87	167.6	12.5
*i*Bu	**8**-SbCl$_6$	7.87	169.0	12.1

^{a} Coupling constant refers to the nitrogen-14 nucleus, see also ref 19. ^{b} Broad, unresolved signals in the proton decoupled carbon-13 spectra.

($\Delta\delta \leq 0.08$ ppm). When compared to the AlCl$_4^-$ compound, this proton becomes more and more deshielded when I$^-$ ($\Delta\delta$ = 0.70 ppm), Br$^-$ ($\Delta\delta$ = 1.11 ppm), or Cl$^-$ ($\Delta\delta$ = 1.42 ppm) are used as counterions (Table 2). A similar but much weaker trend can be observed for the low-field NMe resonance ($\Delta\delta_{max}$ = 0.14 ppm), which is tentatively assigned to the (*E*)-NMe group,[12] whereas the carbon chemical shifts show only little changes and cannot be interpreted straightforwardly.
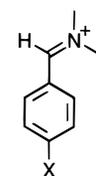
2a$^+$, X = H
2b$^+$, X = OMe

Compared to the cations **1**$^+$, **2a**$^+$, and **2b**$^+$, the $^+N{=}CH_2$ protons of the diethylmethyleneammonium ion **3**$^+$ experience a much weaker deshielding in the presence of halide ions (Table 3). The same NMR spectra as detected for the iminium halides **3**-Cl and **3**-Br have been obtained when the corresponding tetrabutylammonium halides were added consecutively to solutions of the iminium hexachloroantimonate **3**-SbCl$_6$ (Figure 1).

(12) On the basis of earlier NOE experiments with *N,N*-dimethyl(*p*-methylbenzylidene)ammonium tetrafluoroborate reported in ref 44 and our own NOE experiments with **2b**-OTf and **2b**-Cl, it can also be deduced for salts of **2a**$^+$ that the NMe group which resonates at lower field occupies the (*E*)-position of the CN double bond.
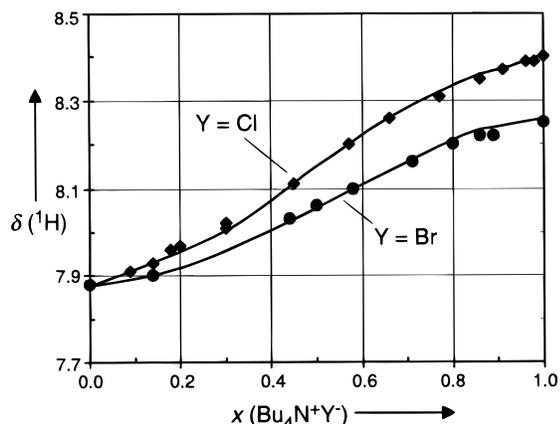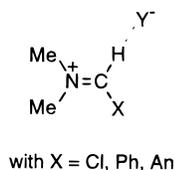
Figure 1. Chemical shift dependence (in CD_3CN) of the $^+N=CH_2$ protons on the mole fraction $x(Bu_4N^+Y^-)$ of 3-$SbCl_6$/$Bu_4N^+Y^-$ mixtures. In the plot the δ value at $x = 0$ refers to a solution of pure 3-$SbCl_6$ while the δ values at $x = 1$ were taken from the ^1H NMR spectra of solutions of pure 3-Cl and 3-Br, respectively.

Scheme 1

with X = Cl, Ph, An

On the other hand, the addition of 8 equiv of $Bu_4N^+Cl^-$ to a solution of 3-Cl did not further affect the chemical shifts of the $=CH_2$ group. We conclude, therefore, that the spectral data given for 3-Cl in Table 3 refer to completely paired iminium ions.

Since ammonium functionalities are known to enhance the hydrogen bond donor abilities of adjacent C_{sp^3}-H[13] and C_{sp^2}-H bonds,[14] we assumed that the iminium halides exist as contact ion pairs with structures as shown in Scheme 1. The formation of $C-H\cdots Y^-$ hydrogen bonds explains that the deshielding of the $^+N=CH(X)$ protons reaches a maximum in the presence of the most basic counterion of this series, i.e. $Y^- = Cl^-$.

Consistent with our model, the diminished influence of the counterion on the NMR spectra of dialkyliminium ions $R_2N^+=CH_2$ can be rationalized by the rapid equilibration shown in eq 4. Due to this degenerate equilibration the observed $\Delta\delta$ for the *two* $=CH_2$ protons reflects only half of the actual deshielding, which is experienced by the proton that participates in the hydrogen bonding. Equation 4 furthermore explains the observed time-averaged C_{2v} symmetry in the NMR spectra of the symmetrically N-substituted methyleneammonium salts (Table 3).

(eq. 4)
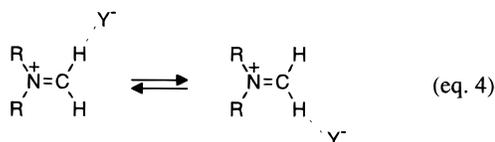
Solvent Dependence. The methine resonance of the iminium ion $2a^+$ remained constant in different aprotic solvents, e.g. in CD_3CN, $CDCl_3$ or CD_2Cl_2 as long as complex counterions ($Y^- = AlCl_4^-$, $SbCl_6^-$, BF_4^-) were employed (Table 4). The corresponding resonance of the iminium *halides*, however, showed

Table 4. Dependence of the $Me_2N^+=CHPh$ ($2a^+$) Proton Resonance on the Solvent

	$\delta(^1H)^a$				
salt	in CD_2Cl_2	in $CDCl_3$	in CD_3CN	in $SO_2{}^b$	in DMSO
2a-Cl	10.65	10.50^c	10.25	8.92	10.02
2a-Br	10.37	10.27	9.94		9.64
2a-I	10.03	9.98	9.53		9.47
2a-OTf	9.10	9.11^d	8.91		9.37
2a-BF_4	8.90^e		8.87		
2a-$SbCl_6$	$-^f$	$-^f$	8.84		9.34
2a-$AlCl_4$	8.85	$-^f$	8.83	8.84	$-^f$

^{a} ^1H NMR spectra (300 MHz) recorded in CD_2Cl_2, $CDCl_3$, DMSO-d_6, and SO_2 refer to tetramethylsilane (δ 0.00), spectra in CD_3CN were referenced to the solvent signal (δ 1.93). ^{b} At -10 °C. ^{c} An identical chemical shift has been reported in ref 42. ^{d} Value taken from ref 9. ^{e} A value of δ 9.01 has been reported for **2a**-BF_4 (in CD_2Cl_2) in ref 44. ^{f} No data could be acquired due to the insolubility of the salts in the solvents.

a strong dependence on the solvent, indicating the different ability of CD_3CN, $CDCl_3$, and CD_2Cl_2 to solvate the anionic moiety: weak solvent−anion interactions cause stronger cation−anion interactions which finally give rise to a higher deshielding of the $^+N=CHPh$ proton.

In CD_3CN, the ^1H NMR resonance of $^+N=CHPh$ ($2a^+$) is deshielded by only 0.08 ppm when $AlCl_4^-$ is replaced by the OTf^- counterion. When the spectra were recorded in CD_2Cl_2, however, this difference increased to 0.25 ppm. The downfield shift of the OTf^- salt indicates that—due to ion pairing—weak hydrogen bonds between the imino proton and the oxygen atoms of the counterion can be formed in the relatively nonpolar solvent CD_2Cl_2.

Since sulfur dioxide is known to be an electron pair acceptor[15] that can be employed as a Lewis acidic solvent,[16] a strong solvation of Cl^- by SO_2 was expected. It was not surprising therefore that solutions of **2a**-Cl ($\delta^+_{N=CHPh}$ 8.92, Table 4) and **2a**-$AlCl_4$ ($\delta^+_{N=CHPh}$ 8.84) in liquid sulfur dioxide exhibit almost identical ^1H NMR spectra: The chemical shifts correspond to those of free ions.

A different behavior was observed for solutions of the iminium salts **2a**-Y in DMSO-d_6. Although the increasing deshielding with growing basicity of the anion was retained qualitatively within the series of the iminium halides, the salts with complex counterions resonated at lower field than in the solvents so far discussed ($\Delta\delta$ +0.5 compared to CD_3CN, Table 4). This phenomenon can be explained by the known hydrogen bond acceptor ability of dimethyl sulfoxide,[17] which probably competes with the anions for the hydrogen-bonding sites of the cations.

Nitrogen-14 NMR. Usually spin−spin coupling to ^{14}N ($I = 1$, 99.6% natural abundance) is not observed due to the rapid quadrupolar interaction which is the predominant relaxation mechanism. Only in a few cases when the high symmetry of the molecule and the partial (or complete) disappearance of the nitrogen lone pair decreases the electric field gradient at the nitrogen site are spin−spin couplings with nuclei like ^1H or ^{13}C as well as narrow ^{14}N NMR linewidths observable.[18]

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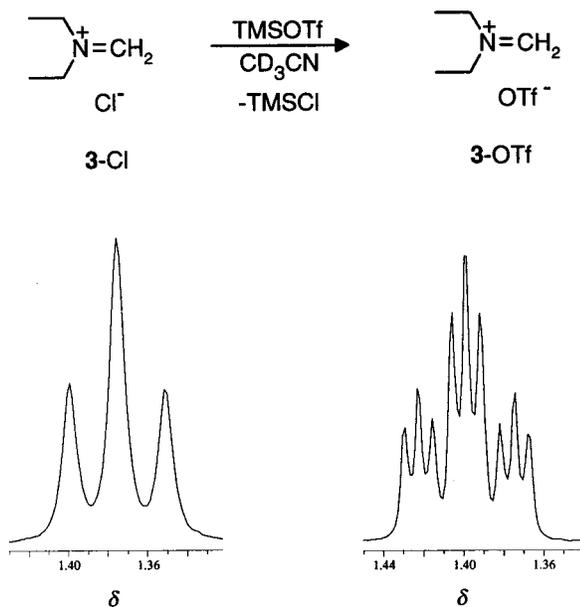
Figure 2. Influence of the counterion on the proton resonance of the methyl group in salts of **3**$^+$ (300 MHz, in CD$_3$CN).

In the ^{1}H NMR spectrum of the *N,N*-diethylmethyleneammonium chloride **3**-Cl, the methyl groups resonate as a broad triplet (Figure 2). Exchange of the counterion by addition of trimethylsilyl triflate (TMSOTf) causes a further splitting due to the coupling with the ^{14}N nucleus ($^3J_{N,H}$ = 2.1 Hz[19]). A well-resolved spectrum with ^{1}H,^{14}N coupling $^3J_{N,H}$ = 2.2 Hz[19] was also observed for the corresponding hexachloroantimonate **3**-SbCl$_6$. This is in accord with earlier reports that $^2J_{N,H}$ became observable in the ^{1}H NMR spectra of *N,N*-dimethylmethyleneammonium salts (**4**-Y) as the nucleophilicity of the counterion decreased.[20]

Since the ^{14}N linewidth is a sensitive probe of the geometry at the nitrogen site, small values are indicators for a highly symmetrical surrounding of the nitrogen nucleus. In solution, the interactions of the iminium cations **3**$^+$−**8**$^+$ with complex counterions seem indeed to be negligible as indicated by the narrow linewidths ($\Delta\nu_{1/2}$ < 7 Hz) of the ^{14}N resonances and the independence of the ^{14}N NMR chemical shifts of the nature of the anions SbCl$_6{}^-$, AlCl$_4{}^-$, and OTf$^-$. The substituent effects on the ^{14}N chemical shift of *N,N*-dialkylmethyleneammonium ions follow a trend similar to that in the corresponding dialkylammonium ions[21] (Figure 3).

Correlation of Chemical Shifts with Thermodynamic Data. The ability of ions to participate in hydrogen bonds should be associated with the single ion free energy for the transfer of an ion from water to acetonitrile $\Delta G_t°$(water → acetonitrile).[22] While $\Delta G_t°$ increases with decreasing size of the halide ions,[22] values for the complex anions which were

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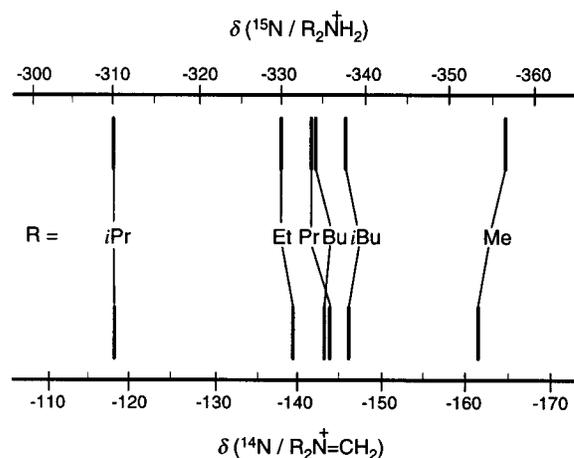
Figure 3. Influence of the *N*-alkyl substituents on the chemical shifts of nitrogen nuclei in dialkylammonium ions[21] and dialkylmethylene-ammonium ions (for ^{14}N NMR chemical shifts of iminium salts, see the Supporting Information).
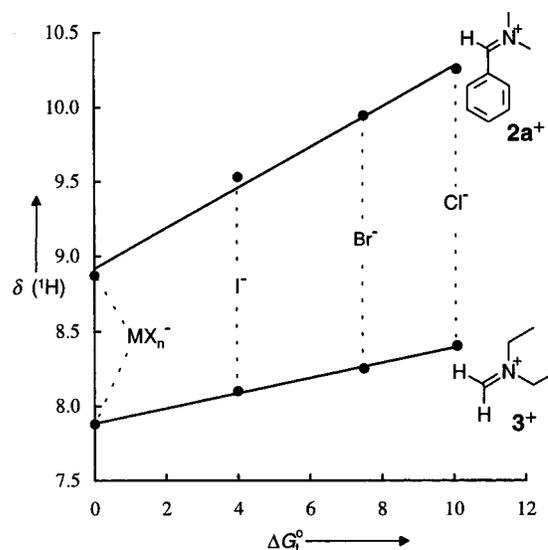

Figure 4. Plot of $\delta(^1$H) of **2a**-Y and **3**-Y in CD$_3$CN vs $\Delta G_t°$ (kcal mol^{-1}) for the transfer of the anions Y$^-$ from water to acetonitrile.

employed in this work have not yet been measured. Since $\Delta G_t°$ for ClO$_4{}^-$ has been determined to be 0.5 kcal mol^{-1},[22] we assumed that the corresponding values of MX$_n{}^-$ = AlCl$_4{}^-$, SbCl$_6{}^-$, and BF$_4{}^-$ are also close to zero. Hence, the correlations of the observed chemical shifts of the iminium ions **2a**$^+$ and **3**$^+$ in acetonitrile-*d*$_3$ with $\Delta G_t°$ of their counterions (Figure 4) are in accord with the postulated interaction between halides and iminium ions via hydrogen bonds.
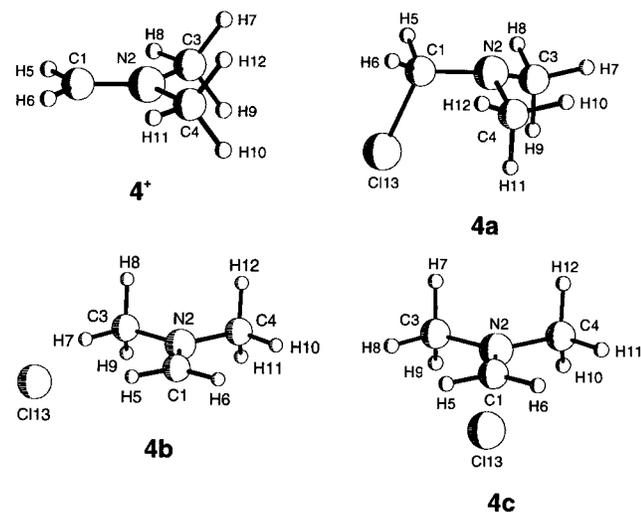
Quantum Chemical Calculations. Inspired by the NMR spectroscopic observation of iminium−halide interactions, we performed quantum chemical calculations[23] on the simplest *N,N*-dialkyliminium chloride, i.e. dimethylmethyleneammonium chloride (C$_3$H$_8$ClN) and its isomers and located three stationary points on the potential energy surface (Table 5, Figure 5). The global minimum **4a** (E_{rel} = 0.0 kcal mol^{-1}; MP2/6-31+G*) corresponds to the covalently bound (chloromethyl)dimethyl-

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Table 5. Ab Initio Total Energies (E), Relative Energies (E_{rel}), Dipole Moments, and Zero-Point Energies (ZPE) for the C$_3$H$_8$ClN Species **4a**−**c**

	4a	**4b**	**4c**
symmetry	C_s	C_s	C_{2v}
RHF/6-31G*//6-31G*			
E/au[a]	−632.17974	−632.14574	−632.13470
E_{rel}/kcal mol^{-1}	0.00	21.33	28.26
dipole moment/D	2.544	14.057	16.168
NIMAG[b]	0	0	1
ZPE/kcal mol^{-1}	75.87	75.09	74.96
MP2/6-31G*//6-31G*			
E/au[a]	−632.86693	−632.81874	−632.80234
E_{rel}/kcal mol^{-1}	0.00	30.24	40.53
RHF/6-31+G*//6-31+G*			
E/au[a]	−632.18361	−632.15283	−632.14335
E_{rel}/kcal mol^{-1}	0.00	19.31	25.26
dipole moment/D	2.556	14.433	16.487
NIMAG[b]	0	0	2
ZPE/kcal mol^{-1}	75.74	75.05	74.89
MP2/6-31+G*//6-31+G*			
E/au[a]	−632.87977	−632.83365	−632.81906
E_{rel}/kcal mol^{-1}	0.00	28.94	38.09

[a] 1 au = 627.49 kcal mol^{-1}. [b] Number of imaginary frequencies (NIMAG): 0 = minimum, 1 = first-order transition state, 2 = second-order transition state on the potential energy surface.

Table 6. Ab Initio Total Energies (E), Relative Energies (E_{rel}), Dipole Moments, and Zero-Point Energies (ZPE) for the Species **4a**−**c** with Two Molecules of Acetonitrile

	4a·2CH$_3$CN	**4b·2CH$_3$CN**	**4c·2CH$_3$CN**
symmetry	C_s	$\sim C_s$	C_{2v}
RHF/3-21G//3-21G			
E/au[a]	−891.46116	−891.45439	−891.44418
E_{rel}/kcal mol^{-1}	0.00	4.25	10.66
dipole moment/D	2.107	6.248	8.098
NIMAG[b]	0	0	3
ZPE/kcal mol^{-1}	139.45	139.34	138.56
RHF/6-31G*//6-31G*			
E/au[a]	−896.04555	−896.03998	−896.03308
E_{rel}/kcal mol^{-1}	0.00	3.50	7.82
dipole moment/D	1.730	6.014	7.742
NIMAG[b]	0	0	3
ZPE/kcal mol^{-1}	138.39	138.36	137.88
MP2/6-31G*//6-31G*			
E/au[a]	−897.54048	−897.53049	−897.52032
E_{rel}/kcal mol^{-1}	0.00	6.27	12.65

[a] 1 au = 627.49 kcal mol^{-1}. [b] Number of imaginary frequencies (NIMAG): 0 = minimum, 3 = third-order transition state on the potential energy surface.

Figure 5. Molecular structures of the cation **4$^+$**, of the covalent compound **4a**, and of the ion pairs **4b** and **4c** (calculational numbering; 6-31+G*//6-31+G*; see also Table 5).

Figure 6. Molecular structures of the acetonitrile solvated isomers **4a·2CH$_3$CN** and **4b·2CH$_3$CN** (calculational numbering; 6-31G*//6-31G*; see also Table 6).

amine which is characterized by a long C−Cl bond (1.868 Å) and a relatively small dipole moment (2.56 Debye).

The second minimum **4b** (E_{rel} = 28.9 kcal mol^{-1}; MP2/6-31+G*) possesses C_s symmetry and corresponds to an ion pair with the chloride ion in the plane of the iminium cation. It shows a large dipole moment (14.4 Debye) and reveals hydrogen bonds from H5 (H5⋯Cl13 = 2.159 Å, C1⋯Cl13 = 3.216 Å, numbering in Figure 5) and, to a lesser extent, from H7 (H7⋯Cl13 = 2.542 Å, C3⋯Cl13 = 3.529 Å) to chloride.
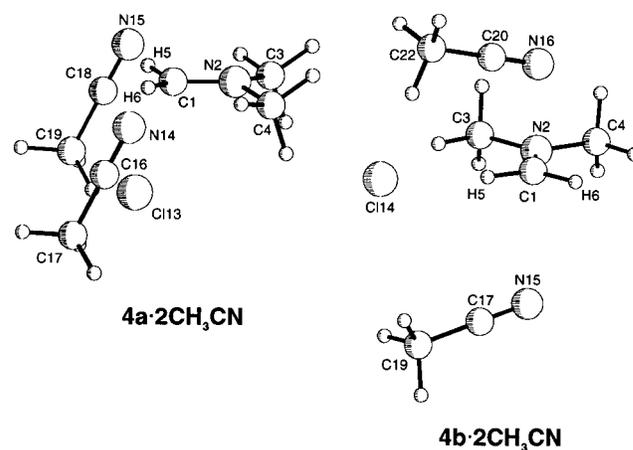
A third stationary point **4c** (E_{rel} = 38.1 kcal mol^{-1}; MP2/6-31+G*) corresponds to a second-order transition state (C_{2v} symmetry) where the chloride is in close contact to both methylene hydrogens H5/H6. When the symmetry constraints are released, chloride moves along the mirror plane perpendicular to the iminium moiety with preservation of the C_s symmetry, and **4c** collapses into the global minimum **4a** without energy barrier.

Comparison of the MP2/6-31+G* energies in Table 5 with the sum of the total energies of the iminium ion **4$^+$** and the chloride ion (E_{rel} = 124.3 kcal mol^{-1}; MP2/6-31+G*)[24] shows

that three-quarters of the energy required to separate **4a** into the free ions in the gas phase are used to overcome the Coulomb attraction between the cation and the anion. Less than one-quarter of the heterolytic bond dissociation energy of **4a** is needed for the rearrangement **4a → 4b**.

These calculations refer to the gas phase and give only a rather crude picture of the behavior in solution. Therefore, we added two molecules of acetonitrile to the three isomeric structures **4a**−**c**, expecting a better approximation of the condensed state from this "super molecule approach".[25] The global minimum (C_s) now corresponds to **4a·2CH$_3$CN** (E_{rel} = 0.00 kcal mol^{-1}; MP2/6-31G*, Table 6, Figure 6), which is in fact an ionized species **4a** plus solvent molecules (C1⋯Cl13 = 2.529 Å). When the C1⋯Cl13 distance is shortened, the relative energy increases without reaching a stationary point.

A second minimum structure **4b·2CH$_3$CN** with a relative energy of 6.3 kcal mol^{-1} (MP2/6-31G*) is derived from the ion pair **4b**. A barrier of 8.3 kcal mol^{-1} is estimated for the

(24) Ab initio total energies of the iminium ion **4$^+$** (−173.010 59 au) and of the chloride ion Cl$^-$ (−459.671 15 au) were calculated on MP2/6-31+G* level (1 au = 627.49 kcal mol^{-1}).

(25) The use of H$_2$O or HCN as model solvents for the calculations was not successful since these protic solvents lead to strong hydrogen bonding to the chloride and weaken its basicity.

Table 7. Calculated ^{13}C and ^{1}H NMR Chemical Shifts for the *N,N*-Dimethylmethyleneammonium Ion **4**$^{+}$, the Contact Ion Pair **4b**, and the Covalent Compound **4a** (Atom Numbering, See Figure 5)

method[a]	$\delta($**4**$^{+})$		$\delta($**4b**$)$		$\delta($**4a**$)$	
	A	B	A	B	A	B
symmetry	C_{2v}	C_{2v}	C_s	C_s	C_s	C_s
C1	169.04	181.76	183.13	192.62	70.79	85.88
C3	45.11	48.25	40.84	42.81	36.24	38.63
C4	45.11	48.25	43.78	46.67	36.24	38.63
H5	8.19	8.22	12.65	16.34	4.64	5.18
H6	8.19	8.22	7.93	8.19	4.64	5.18
H7	3.89	3.81	6.74	8.25	2.18	2.19
H8	3.86	3.88	2.81	2.67	2.18	2.23
H9	3.89	3.81	2.81	2.67	2.43	2.55
H10	3.89	3.81	3.21	3.22	2.18	2.19
H11	3.86	3.88	3.33	3.26	2.43	2.55
H12	3.89	3.81	3.33	3.26	2.18	2.23

[a] Method A: RHF/6-31+G*//6-31+G*. Method B: RHF/6-311+G(2d,p)//B3LYP/6-31G*.

interconversion of the two solvated structures **4a·2CH₃CN** and **4b·2CH₃CN**. Thus, even the very simple solvent model with two molecules of acetonitrile indicates the possibility of an equilibrium of both species which can be expected to be shifted even further to the ion pair structure **4b** when additional solvent molecules are present.

Solvation of the transition state **4c** does not give rise to a minimum structure but to a transition state of third order (NIMAG = 3, E_{rel} = 12.7 kcal mol^{-1}; MP2/6-31G*) that relaxes to structure **4a·2CH₃CN** when the symmetry constraints are released.

Because of the ionic nature of both **4a·2CH₃CN** and **4b·2CH₃CN** calculated for the gas phase, it is not surprising that dialkyliminium chlorides are ionic in the condensed phase and that the crystal structure of *N,N*-dimethylmethyleneammonium chloride closely resembles structure **4b** (or **4b·2CH₃CN**) with the chloride ion in the (N−C−H) plane.[26]

In order to interpret the observed NMR chemical shifts, we have performed quantum chemical calculations for the free iminium ion **4**$^{+}$, the contact ion pair **4b**, and the covalent chloromethylamine **4a** using the GIAO method[27] on two levels of theory. It is obvious that the change from the iminium ion **4**$^{+}$ to the covalent molecule **4a** is associated with a significant shielding of ^{13}C and ^{1}H of the $^{+}$N=CH₂ group[28] (C1 and H5/H6, respectively, Table 7). Such a trend was not observed experimentally when changing from iminium salts with weakly nucleophilic counterions, e.g. **3**-SbCl₆, to **3**-Cl (Table 3). The GIAO calculations furthermore show—in accord with our experimental observations—that the change from the free ion **4**$^{+}$ to the ion pair **4b** results in the deshielding of the proton H5 which is involved in the hydrogen bond to Cl^{-}. However, the magnitude of this shift is predicted differently by the two employed methods of theory (Table 7).

Conclusions

Extensive work on the kinetics of the reactions of carbocations with nucleophiles has shown that the second-order rate constants were independent of the nature of the complex counterions.[2,29] This phenomenon was explained by the fact that the cation−

anion interactions were exclusively electrostatic, and because they were of comparable magnitude in the ground and the transition state, variations of the counterions did not affect the rates.[2,29] Due to the low stabilization of the carbocations used for those investigations, only complex anions have been employed; in the presence of free halide ions coordination with the carbocations to give covalent products would have taken place.

The situation is different for iminium salts. As discussed above, the stabilization of the positive charge by the nitrogen lone pair is so strong that ordinary iminium chlorides, bromides, and iodides are ionic in many solvents, and it has been reported that iminium ions with different counterions give different products in reactions with alkynes and allylsilanes.[30] This study has shown that specific cation−anion interactions in iminium halides (C−H···Hal^{-} hydrogen bonds) may be responsible for these observations.

Since the pioneering work of Allerhand and Schleyer,[31] the hydrogen bond donor abilities of CH groups have intensively been studied. 1,3-Dialkylimidazolium ions[32−34] are the only carbocation analogues which have previously been observed to behave as CH hydrogen bond donors. In the neat melts of these salts, the proton NMR chemical shifts of the cationic moieties are strongly affected by the nature of the counterions, which has been assigned to the formation of C−H···Y^{-} hydrogen bonds. Although the exact structure of the contact ion pairs in ionic liquids has been subject of controversal discussion for more than one decade,[32] the X-ray analysis of 1-ethyl-3-methylimidazolium iodide[35] and NMR studies of solutions of further 1,3-dialkylimidazolium salts in aprotic solvents[32,36] indicate that the strongest C−H···Y^{-} hydrogen bonds are formed to ring carbon 2.

Analogously, hydrogen-bonding abilities of the triflate ion have been reported for the positively charged tungsten vinyl ether complex [Cp(CO)₃W(η^2-EtOCH=CHCH₃)]$^{+}$.[37] The results of the X-ray structure analysis revealed evidence for a network of C−H···O hydrogen bonds[38] between the cationic tungsten complex and the OTf^{-} counterion, and a downfield shift of the Cp (0.13 ppm) and the vinyl protons (0.5 ppm for EtOCH) in the presence of OTf^{-} compared to BAr₄$^{-}$ [Ar = 3,5-bis(trifluormethyl)phenyl] was observable in the NMR spectra of CD₂Cl₂ solutions. As a parallel to our results (Table 4), these chemical shift differences disappeared (<0.03 ppm) in CD₃CN solution.

As expected from these literature reports, hydrogen bonding also plays an important role in iminium halides, and it has been

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shown in this work that C−H···Hal⁻ bonds rather than equilibria between ionic and covalent moieties are responsible for the anion dependence of the NMR chemical shifts of iminium ions. It remains to be clarified whether there is a systematic relationship between the strengths of the hydrogen bonds and the reactivities of iminium ions.

Experimental Section

NMR Experiments. The storage of the iminium salts and of the deuterated solvents as well as the sample preparation for the NMR measurements were carried out in a glovebox under argon atmosphere. The deuterated solvents were used as purchased, and sulfur dioxide gas was dried with P_2O_5 before its condensation. NMR data were collected with Bruker WM 300 or ARX 300 spectrometers. ¹H NMR spectra (300 MHz) of solutions in CD_2Cl_2, $CDCl_3$, dimethyl sulfoxide-d_6 (DMSO), and sulfur dioxide were calibrated to tetramethylsilane (δ_H 0.00) whereas solutions in acetonitrile-d_3 refer to the solvent signal (δ_H 1.93). ¹³C NMR spectra (75.5 MHz) refer to acetonitrile-d_3 (δ_C 1.30). DEPT-135 experiments were used to get information about the multiplicity of ¹³C resonances. Proton-decoupled ¹⁴N NMR spectra of iminium salts (0.5 M in acetonitrile-d_3) were recorded on the Bruker ARX 300 spectrometer (21.7 MHz) in NMR tubes with 5 mm diameter and refer to nitromethane (δ_N 0.0) as external standard. For the determination of half-height linewidths $\Delta\nu_{1/2}$, the spectra were processed with the deconvolution routine (Lorentzian-type curve fitting) of the program WIN-NMR by Bruker.

Chemicals. Vilsmeier salts **1**-AlCl₄[39] and **1**-SbCl₆[40] were prepared from commercially available **1**-Cl (Fluka) as reported in the literature. The benzylideneammonium salts **2a**-Cl, **2a**-Br, **2a**-AlCl₄, **2a**-SbCl₆, and **2b**-Cl were synthesized according to Risch's method[41,42] from the corresponding aminals. The preparation of **2a**-I was described by Böhme;[43] that of **2a**-BF₄ by Leonard.[44] In analogy to known procedures[45−47] diethylmethyleneammonium chloride (**3**-Cl), bromide (**3**-Br), and iodide (**3**-I) were obtained from reactions of diethyl-(methoxymethyl)amine[45] with chlorotrimethylsilane (Merck-Schucha-rdt), bromotrimethylsilane (Aldrich), and iodotrimethylsilane (Merck-Schuchardt), respectively, in dichloromethane. Starting from **4**-Cl (Merck-Schuchardt), the procedure of Knoll and Krumm[20] was employed to yield **4**-AlCl₄ and **4**-SbCl₆.

Iminium Triflates. The compounds **1**-OTf, **2a**-OTf,[9] **2b**-OTf, **3**-OTf, and **4**-OTf were generated under argon atmosphere in rubber-septum-equipped NMR tubes by addition of 1.5 equiv of trimethylsilyl triflate (Fluka) to a solution of the corresponding iminium chloride in the deuterated solvent.[48]

General Procedure for the Generation of Dialkylmethyleneammonium Hexachloroantimonates. One equivalent of chlorotrimethylsilane was added to a stirred solution of the corresponding (alkoxymethyl)dialkylamine[45] in dichloromethane (1−5 mL/mmol). After 30 min the colorless solution was cooled with an ice bath. Careful addition of 1 equiv of antimony(V) chloride (Merck-Schuchardt) was followed by another 15 min of stirring without cooling. The iminium hexachloroantimonates precipitated from the solutions, were isolated by filtration with suction, washed twice with a dichloromethane/diethyl ether mixture (1/1, v/v), dried in vacuo, and stored under argon. The thus obtained salts were analytically pure without further purification. For spectroscopic data (¹H, ¹³C, and ¹⁴N NMR, IR) and results of elemental analyses, see the Supporting Information.

Supporting Information Available: Elemental analyses and NMR and IR data of iminium hexachloroantimonates, results of nitrogen-14 NMR measurements, and details concerning the quantum chemical calculations (GAUSSIAN 94 Archive Entries) (5 pages). See any current masthead page for ordering and Internet access instructions.

JA972860U

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