The Proton Affinities of Imines and the Heats of Formation of Immonium Ions Investigated with Composite ab Initio Methods

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Abstract: Heats of formation of aliphatic imines and immonium ions calculated with the G2(MP2) and CBS-Q composite ab initio methods are in reasonable agreement with experimentally determined literature values, particularly when the 298 K heats of formation of immonium ions are rederived from threshold energy measurements with inclusion of the 298 K enthalpy contributions proposed by Traeger and McLoughlin. The heats of formation calculated with the simplified procedures, G2(MP2,SVP) and CBS-q, can deviate significantly from the G2(MP2) and CBS-Q results, whereas the four methods yield very similar proton affinities. The increase in proton affinity brought about by the introduction of substituents at the imine carbon is substantial, masking any effects of the nitrogen atom hybridization. Cis imines are more basic than their trans isomers, which reflects that the energy difference between cis and trans isomers of imines is unusually high, 15−17 kJ mol^{-1}. Protonation of imines changes the energy difference between the favored, eclipsed conformers. A Benson-type additivity scheme for the heats of formation of immonium ions is proposed, and new group additivity values for imines are determined.

A considerable number of experimental studies of the influence of substituents and hybridization on the proton affinity (PA) of nitrogen-containing molecules have appeared, with much of the early work summarized in the review by Aue and Bowers.[1] Their work included results for a small number of aliphatic imines, but experimental studies of this class of compound have not been common, in part because simple imines are prone to undergo condensation and polymerization reactions.[2] These problems can be circumvented to some extent by examining the deprotonation of immonium ions (eq 1), and the proton affinities of a few simple imines were recently determined in this manner.[3,4] However, a comprehensive study of imine proton affinities and heats of formation has not appeared.

$$RCH=NHR^+ + B \rightleftarrows RCH=NR + BH^+ \qquad (1)$$

The situation is somewhat better with regard to the heats of formation of aliphatic immonium ions. Lossing, Lam, and Maccoll[5] determined the heats of formation of immonium ions with up to three carbon atoms, but data for larger species are, in most cases, not available.

Recent work has demonstrated that reliable proton affinities and heats of formation can be determined computationally with composite ab initio methods of the G2 and CBS families.[6−15]

In the present study, we have used the G2(MP2)[7] and CBS-Q[10] methods to calculate the proton affinities of aliphatic imines and the 0 and 298 K heats of formation of imines and immonium ions with up to four carbon atoms and several with five, to establish an internally consistent set of values for these compounds. Results were also obtained with the G2(MP2,SVP),[8] CBS-q, and CBS-4[10] methods, to examine whether these computationally less demanding procedures would be useful alternatives in studies of larger imines or immonium ions. Our results for the heats of formation of imines complement and extend the G2 calculations published by Seasholtz and co-workers,[16] whereas no systematic computational studies of immonium ions have appeared.

Seasholtz et al.[16] derived Benson group additivity values for aliphatic imines from the G2 heats of formation of imines with up to three carbon atoms. We have used the present more extensive set of heats of formation to revise and extend their results. A number of predictive schemes have been proposed[17−19] to estimate the heats of formation of a variety of radical cations,

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and Maccoll[20] proposed a simple equation to relate the heats of formation of immonium ions to the heats of formation of alkyl cations. The heats of formation of the 35 immonium ions included in this investigation allow us to derive group additivity values for aliphatic immonium ions; to our knowledge, this constitutes the first Benson-type additivity scheme for ionic species.

Methods

Heats of Formation. The proton affinities and heats of formation were derived from G2(MP2),[7] G2(MP2,SVP),[8] CBS-Q, and CBS-q[10] total energies calculated with the Gaussian 94 program package[21] (Tables S1 and S2 in the Supporting Information).

The 0 K heats of formation were calculated via atomization energies[22] as described by Nicolaides et al.[23] (eq 2); as recommended by these authors, the experimentally determined heats of formation for the constituent atoms[24] were used in the calculation.

$$\Delta H^\circ_{f,0}(M) = E(M, 0\ K) - \sum E(\text{atoms}, 0\ K) + \sum \Delta H^\circ_{f,0}(\text{atoms}) \quad (2)$$

In the calculation of 298 K heats of formation from the 0 K values (eq 3), we used the integrated heat capacity of the molecules in question derived from the scaled HF/6-31G(d) frequencies and the experimentally determined integrated heat capacities of the elements involved.[24]

$$\Delta H^\circ_{f,298}(M) = \Delta H^\circ_{f,0}(M) + \int C_p(M)\ dT - \sum \int C_p(\text{elem})\ dT \quad (3)$$

The values obtained in this manner (Tables 1 and 4) correspond, for ionic species, to experimental values derived using the stationary electron convention. The harmonic oscillator approximation was used for all vibrational frequencies in the calculation of the integrated heat capacity. A number of recent studies[13,15,16] have argued that the calculated 298 K heats of formation are often not significantly improved by considering low-frequency vibrations as torsions.

Proton Affinities. The proton affinity is defined[19] as an enthalpy change at 298 K and may be calculated from the 298 K heats of formation of the species involved (eq 4).

$$PA = \Delta H^\circ_{f,298}(M) - \Delta H^\circ_{f,298}(MH^+) + \Delta H^\circ_{f,298}(H^+) \quad (4)$$

Introduction of the heats of formation as expressed by eqs 2 and 3 into eq 4 yields eq 5, which makes it possible to obtain the proton affinity directly from the calculated 0 K total energies and the calculated integrated heat capacities of the molecule and the protonated molecule. The results in Table 8 were obtained in this manner.

The heat capacity terms in eq 5 are sometimes omitted in proton affinity calculations in the literature, which implicitly introduces the

$$PA = E(M, 0\ K) + \int C_p(M)\ dT - E(MH^+, 0\ K) -$$

$$\int C_p(MH^+)\ dT + {}^5/_2 RT \quad (5)$$

simplifying assumption that protonation does not change the heat capacity significantly. For the compounds included in the present study, making this assumption would change the calculated proton affinities by 1 kJ mol^{-1} or less. We note that eq 4 should not be used with heats of formation of M or MH$^+$ derived from calculations with simplified composite methods such as CBS-q, since the values for $\Delta H^\circ_f(H^+)$ obtained with these methods differ considerably from that determined experimentally.

Group Additivity Values. The group additivity values for imines (Table 2) and immonium ions (Table 6) were determined by a least-squares fit of the contributions from each of the constituent groups to the 298 K G2(MP2) heats of formation of the imines and immonium ions examined. The fitting procedure involves solution of a linear least-squares problem with more equations than unknowns. We used the singular value decomposition method described by Press et al.[25]

Following Benson,[26] we assign the same value to methyl groups bonded directly to the C=N groups as to other CH$_3$ groups. The values used for these and for methylene groups in aliphatic chains are Cohen and Benson's 1992 values.[27] For imines as well as for immonium ions, we use Benson's assignment[28] for the doubly bonded CH$_2$ contribution, the same value as that for a terminal alkene CH$_2$.

Results and Discussion

Heats of Formation of Imines. The heats of formation of imines obtained with the G2(MP2) method are slightly lower than those derived from the CBS-Q calculations (average difference 3 kJ mol^{-1}, maximum difference 5 kJ mol^{-1}; see Table 1). A similar trend can be found in the results reported by Ochterski et al.[11] and by ourselves.[14] The G2(MP2,SVP) results lie lower than the G2(MP2) results, and the difference between the two sets of results increases with the size of the imine (average -3 kJ mol^{-1} for C$_1$ and C$_2$ imines, -5 kJ mol^{-1} for C$_3$ imines, -7 kJ mol^{-1} for C$_4$ imines). The CBS-Q and CBS-q results are quite similar, with the exception of imines with a fully substituted imine carbon atom. The heats of formation obtained with the CBS-4 method (not included in Table 1) are up to 20 kJ mol^{-1} lower than those obtained with CBS-q.

The results of experimental studies of the 298 K heats of formation of the three C$_1$ and C$_2$ imines reported in the literature were summarized by Seasholtz et al.;[16] a limited number of experimental values for higher imines are included in authoritative compilations,[19,28] and a critical review and overview of imine thermochemistry was recently presented by Slayden and Liebman.[29] The agreement between the published results and our calculated heats of formation is reasonable (Table 1). Wiberg et al.[30] used isodesmic substitution calculations to predict heats of formation for five simple imines; their values are well reproduced by the present results. Our G2(MP2) heats of

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(22) Our calculated atom energies are identical to those reported for the G2(MP2) and G2(MP2, SVP) procedures (refs 7 and 8) and for the CBS-Q method (refs 10 and 11), except for a 0.03 mH difference for the oxygen atom CBS-Q energy.

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Table 1. Heats of Formation of Imines[a]

	exp,[b] 298 K	isod,[c] 298 K	G2(MP2) 0 K	G2(MP2) 298 K	G2(MP2,SVP), 298 K	CBS-Q, 298 K	CBS-q, 298 K
$CH_2=NH$	88[d]	86	95	87[e]	85	92	93
E-$CH_3CH=NH$	33[f]	40	58	43	39	47	45
Z-$CH_3CH=NH$			60	46	42	50	49
$CH_2=NCH_3$	72[g]	77	94	79	76	84	86
E-$CH_3CH_2CH=NH$[h]			45	24	18	28	26
Z-$CH_3CH_2CH=NH$			49	28	23	32	30
$(CH_3)_2C=NH$			23	2	−4	5	−2
E-$CH_3CH=NCH_3$		33	57	36	31	40	40
Z-$CH_3CH=NCH_3$		51	73	53	48	57	58
$CH_2=NCH_2CH_3$[i]			74	53	48	58	58
E-$CH_3CH_2CH_2CH=NH$[j]			32	5	−3	7	5
Z-$CH_3CH_2CH_2CH=NH$			35	8	1	10	7
E-$(CH_3)_2CHCH=NH$			25	−2	−10	0	−2
Z-$(CH_3)_2CHCH=NH$			29	1	−7	3	1
E-$CH_3CH_2(CH_3)C=NH$			9	−17	−25	−16	−21
Z-$CH_3CH_2(CH_3)C=NH$			10	−17	−25	−17	−21
E-$CH_3CH_2CH=NCH_3$			44	17	10	20	20
Z-$CH_3CH_2CH=NCH_3$			61	35	27	38	39
$(CH_3)_2C=NCH_3$			34	9	2	11	8
E-$CH_3CH=NCH_2CH_3$[k]	18[l]		37	10	3	13	12
Z-$CH_3CH=NCH_2CH_3$			52	26	19	29	30
$CH_2=NCH_2CH_2CH_3$			60	32	25	37	36
$CH_2=NCH(CH_3)_2$			46	19	12	23	20
$CH_3CH_2(CH_3)CHCH=NH$			10	−23	−33	−22	−24
E-$CH_3CH_2CH=NCH_2CH_3$	0,[g] 3[m]		24	−9	−19	−7	−9
Z-$CH_3CH_2CH=NCH_2CH_3$			40	7	−2	10	9
$(CH_3)_2C=NCH_2CH_3$	−36[l]		12	−20	−29	−19	−21
E-$CH_3CH=NCH_2CH_2CH_3$	−5,[g] −2[m]		23	−10	−19	−9	−11
$CH_2=NCH(CH_3)CH_2CH_3$			31	−2	−12	0	−3

[a] Heats of formation in kJ mol^{-1}. The same $\Delta H°_{f,298} - \Delta H°_{f,0}$ difference was obtained for all four methods. [b] Preferred values, see refs 16 and 29 for summaries of literature results. [c] Calculated by isodesmic substitution (ref 30). [d] From ref 43. [e] G2 calculations by Smith et al. (ref 44) yielded a value of 86 kJ mol^{-1}. [f] The heat of formation reported in ref 3 was reevaluated, taking $\Delta H°_{f,298}(CH_3CH=NH_2^+)$ to be 666 kJ mol^{-1} (this work). [g] From ref 28. [h] NCCC dihedral angle of 0°; $\Delta H°_{f,298}$ of the conformer with an NCCC angle of 120° is 26, 29 kJ mol^{-1} [G2(MP2), CBS-Q]. [i] CNCC dihedral angle of 120°; $\Delta H°_{f,298}$ of the conformer with a CNCC angle of 0° is 60, 64 kJ mol^{-1} [G2(MP2), CBS-Q]. [j] NCCC dihedral angle of 0°; $\Delta H°_{f,298}$ of the conformer with an NCCC angle of 120° is 6, 7 kJ mol^{-1} [G2(MP2), CBS-Q]. [k] CNCC dihedral angle of 120°; $\Delta H°_{f,298}$ of the conformer with a CNCC angle of 0° is 18, 21 kJ mol^{-1} [G2(MP2), CBS-Q]. [l] From ref 19. [m] From ref 29.

formation of imines are almost the same as those derived from G2 calculations by Seasholtz et al.[16]

The introduction of methyl groups on the nitrogen atom of the imine lowers the heat of formation by about 8 kJ mol^{-1} in the absence of steric interactions, whereas the available data[31] suggest that introduction of *N*-methyl groups in saturated amines often only changes the heat of formation marginally.[32] Methyl substitution at the imine carbon atom causes a much larger change, −40−45 kJ mol^{-1}. This change is more pronounced than that found upon methyl substitution at alkene double bonds but somewhat less pronounced than that observed for carbonyl compounds, suggesting that the C=N group in imines is less polarized than is the C=O group in aldehydes and ketones.

Steric and Conformational Factors. The calculated heats of formation of highly substituted imines show that steric effects influence the imine thermochemistry significantly. Table 1 includes the heats of formation of several pairs of cis/trans isomeric imines. When a hydrogen atom and an alkyl group are involved, the trans-form (also denoted *E* or anti in the literature) is lower in energy by 2−3 kJ mol^{-1}, in good agreement with the results of experimental studies[33] and previous calculations.[34] When two alkyl groups are involved, the trans-

Figure 1. Preferred eclipsed conformations of imines. (a) Methyl group in C=N plane; (b) H in C=N plane.

form is more stable by 15−17 kJ mol^{-1}. This energy difference is considerably larger than that found for immonium ions or for alkenes, e.g., the cis/trans energy differences for CH_3-$CH=NCH_3$, $CH_3CH=NHCH_3^+$, and $CH_3CH=CHCH_3$ are 17, 7, and 4 kJ mol^{-1}. The reason cis-imines are destabilized to this extent is not yet clear.

The lower-energy conformation of imines with two-carbon or longer chains on the imine carbon atom is one in which the β-carbon atom eclipses the =NR group (NCCC dihedral angle close to 0°; Figure 1a). NMR studies by Karabatsos and coworkers[35,36] showed that this conformation predominates in the condensed phase, and Dorigo, Pratt and Houk[37] discussed possible reasons why the eclipsed conformations are preferred. For both $CH_3CH_2CH=NH$ and $CH_3CH_2CH_2CH=NH$, we find the energy difference between this conformation and that in which a hydrogen eclipses the C=N to be quite small, close to

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(32) The data for the few *N*-methylated amines reported in ref 31 include results that have not been published (Liebman, J. F., personal communication); however, the apparent trend is confirmed by preliminary G3 calculations which show that *N*-methylation of methylamine, ethylamine, and propylamine causes a slight *increase* in the 298 K heat of formation (about 4 kJ mol^{-1}).

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Table 2. Group Additivity Values for Imines[a]

$N_{im}H$	60.5	$C_{im}-(C,H)$	24.8
$N_{im}-(C)$	95.2	$C_{im}-(2C)$	21.7
$CH_2-(N_{im},C)$	−26.8	$CH_2-(C_{im},C)$	−18.6
$CH-(N_{im},2C)$	−18.8	$CH-(C_{im},2C)$	−3.8
$CH_3-(N_{im})$	−41.8[b]	$CH_3-(C_{im})$	−41.8[b]
$CH_3-(C)$	−41.8[b]	$CH_2-(2C)$	−20.9[b]
$C_{im}H_2$	26.2[c]	*cis*-CH correction	3.2[d]
cis-CC correction	16.5[e]		

[a] Values in kJ mol^{-1}. [b] Assigned (ref 27). [c] Assigned to be the same as C_dH_2 (ref 28). [d] The *cis*-CH correction applies when the *N*-hydrogen is cis with respect to a *C*-alkyl group. [e] The *cis*-CC correction applies when two alkyl groups on the C=N double bond are cis with respect to each other.

1 kJ mol^{-1}; the difference increases upon protonation (see immonium ions, below). Eclipsed conformations are also preferred for *N*-alkyl-substituted imines, but the lower-energy conformer is here one where hydrogen rather than carbon eclipses the N=C group (CNCC dihedral angle close to 120°; Figure 1b). The energy difference between the eclipsed conformers is considerably higher for *N*-alkyl imines than for *C*-alkyl imines; for $CH_2=NCH_2CH_3$ and $CH_3CH=NCH_2CH_3$, we find a difference of 7−8 kJ mol^{-1}.

Group Additivity Values for Imines. The results for the 29 imines included in the present study enable us to extend the additivity scheme suggested by Seasholtz et al.[16] and to suggest revised group additivity values. All groups for which values are required are present more than once in the set of imines examined. Use of the revised scheme (Table 2) to estimate the heats of formation of imines yields results that are within 1.3 kJ mol^{-1} of the G2(MP2) values (Table 3).

Heats of Formation of Immonium Ions. The composite ab initio methods compare for immonium ions much as they do for imines. The CBS-Q heats of formation are up to 6 kJ mol^{-1} higher than those obtained with the G2(MP2) method (average, +4 kJ mol^{-1}); however, this difference appears to decrease with the number of carbon atoms (Table 4). The G2(MP2,SVP) results lie lower than the G2(MP2) results, with a maximum deviation of 7 kJ mol^{-1}; this difference increases with the number of carbon atoms. The difference between the CBS-Q and CBS-q heats of formation increases with substitution on the nitrogen atom, e.g., the differences for $CH_2=NH_2^+$, $CH_2=NHCH_3^+$, and $CH_2=N(CH_3)_2^+$ are 6, 9, and 13 kJ mol^{-1}, respectively. The CBS-4 method yields immonium ion heats of formation (not included in Table 4) that in many cases agree reasonably with the G2(MP2,SVP) results, but the deviations encountered can be relatively large, and they are not obviously systematic.

The experimental 298 K heats of formation of aliphatic immonium ions with up to three carbon atoms were determined by Lossing et al.,[5] who used appearance energy measurements after ionization by energy-selected electrons; the possible error was estimated to be ±8 kJ mol^{-1}. A comparison of our results with Lossing's results shows that many of the immonium ion heats of formation calculated with the composite ab initio methods (Table 4) are outside the usual ±10 kJ mol^{-1} target accuracy: the G2(MP2) results are up to 18 kJ mol^{-1} higher than Lossing's values, with an average difference of +10 kJ mol^{-1}, and the CBS-Q results lie yet higher, between 5 and 23 kJ mol^{-1} above Lossing's values (average, +15 kJ mol^{-1}).

The agreement between the 298 K heats of formation derived from Lossing's appearance energy measurements and our calculated values is considerably improved if Traeger and McLoughlin's 298 K enthalpy contributions[38] are taken into account (eq 6) when the reported threshold energy measure-

ments[5] are converted to 298 K heats of formation. The auxiliary thermochemical information used is collected in Table 5, and the revised experimental values are included in Table 4.

$$M \rightarrow D^+ + N \qquad (6)$$
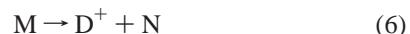
$$\Delta H^\circ_{f,298}(D^+) = AE(D^+) + \Delta H^\circ_{f,298}(M) - \Delta H^\circ_{f,298}(N) + \int C_p(D^+)\,dT + \int C_p(N)\,dT - {}^5\!/_2 RT$$

Heats of formation are derived from threshold energy measurements on the premise that the reverse reaction, in this case the addition of alkyl radicals to immonium ions, proceeds without an appreciable energy barrier. This assumption may not always be valid,[39] and when failing, the derived heats of formation will be too high. Our calculations suggest that this may be the case for $CH_3CH_2CH=NH_2^+$ and $(CH_3)_2C=NH_2^+$. Experimental evidence has been presented to show that formation of the latter ion by α-cleavage of the *tert*-butylamine radical cation is indeed accompanied by an energy barrier in excess of the reaction endothermicity.[39] We take the observation that our calculated heat of formation of $(CH_3)_2C=NH_2^+$ and the value reported by Lossing[5] are almost the same to indicate that, in this case, the 298 K enthalpy contributions and the energy barrier are fortuitously of the same magnitude.

The introduction of a methyl group on the carbon atom of the $C=N^+$ group lowers the heat of formation by approximately twice as much as does introduction of a methyl group on the nitrogen atom. This suggests that a considerable fraction of the positive charge is located on carbon. The effect of a second methyl group on nitrogen or on carbon is slightly lower than the effect of the first. As pointed out by Lossing et al.,[5] the stabilization caused by introduction of substituents at the doubly bonded carbon is less pronounced for immonium ions than for the corresponding oxonium ions derived from aldehydes and ketones, suggesting that the aminocarbonium ion canonical structure is less appropriate for immonium ions than is the hydroxycarbonium ion for oxonium ions.

$$>C=OH^+ \leftrightarrow >C^+-OH \qquad >C=NH_2^+ \leftrightarrow >C^+-NH_2$$

Maccoll[20] suggested that the appearance energy for methyl loss from the diethylamine molecular ion was sufficiently low as to indicate that rearrangement accompanied α-cleavage, to yield a $C_3H_8N^+$ isomer more stable than $CH_2=NHCH_2CH_3^+$. Our results do not lend support to this suggestion.

Steric and Conformational Factors. The preferred conformations of immonium ions with two-carbon or longer substituents on the C=N carbon are eclipsed. Experimental studies have shown that a similar arrangement is preferred for carbonyl compounds and for imines;[36,40] the present results indicate that the energy difference between the eclipsed conformers is particularly pronounced for immonium ions. The conformation of $CH_3CH_2CH=NH_2^+$ in which the β-carbon atom eclipses the C=N group (NCCC dihedral angle close to 0°; Figure 2a) is 5 kJ mol^{-1} lower in energy than that in which a hydrogen atom is the eclipsing atom (NCCC dihedral angle close to 120°). The energy difference between the eclipsed conformers does not change much upon N-substitution ($CH_3CH_2CH=NHCH_3^+$, 5

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Table 3. Heats of Formation of Imines Calculated by Additivity[a]

	add[b]	diff[c]		add[b]	diff[c]		add[b]	diff[c]
CH$_2$=NH	87[e]	0	E-CH$_3$CH$_2$CH$_2$CH=NH	4	−1	Z-CH$_3$CH=NCH$_2$CH$_3$	26	0
E-CH$_3$CH=NH	44	1	Z-CH$_3$CH$_2$CH$_2$CH=NH	7	−1	CH$_2$=NCH$_2$CH$_2$CH$_3$	32	0
Z-CH$_3$CH=NH	47	1	E-(CH$_3$)$_2$CHCH=NH	−2	0	CH$_2$=NCH(CH$_3$)$_2$	19	0
CH$_2$=NCH$_3$	80	1	Z-(CH$_3$)$_2$CHCH=NH	1	0	CH$_3$CH$_2$(CH$_3$)CHCH=NH	−23	0
E-CH$_3$CH$_2$CH=NH	25	1	E-CH$_3$CH$_2$(CH$_3$)C=NH	−17	0	E-CH$_3$CH$_2$CH=NCH$_2$CH$_3$	−9	0
Z-CH$_3$CH$_2$CH=NH	28	0	Z-CH$_3$CH$_2$(CH$_3$)C=NH	−17	0	Z-CH$_3$CH$_2$CH=NCH$_2$CH$_3$	8	1
(CH$_3$)$_2$C=NH	2	0	E-CH$_3$CH$_2$CH=NCH$_3$	18	1	(CH$_3$)$_2$C=NCH$_2$CH$_3$	−19	1
E-CH$_3$CH=NCH$_3$	36	0	Z-CH$_3$CH$_2$CH=NCH$_3$	34	−1	E-CH$_3$CH=NCH$_2$CH$_2$CH$_3$	−11	−1
Z-CH$_3$CH=NCH$_3$	53	0	(CH$_3$)$_2$C=NCH$_3$	8	−1	CH$_2$=NCH(CH$_3$)CH$_2$CH$_3$	−2	0
CH$_2$=NCH$_2$CH$_3$	53	0	E-CH$_3$CH=NCH$_2$CH$_3$	10	0			

[a] Values in kJ mol^{-1}; group additivity values in Table 2. [b] Value calculated by additivity. [c] ΔH_f°[additivity] − ΔH_f°[G2(MP2)].

Table 4. Heats of Formation of Immonium Ions[a]

	exp, 298 K		G2(MP2)[d]		G2(MP2,SVP), 298 K	CBS-Q, 298 K	CBS-q, 298 K
	lit.[b]	rederiv[c]	0 K	298 K			
CH$_2$=NH$_2$$^+$	745	752[e]	761	749	749	754	760
CH$_3$CH=NH$_2$$^+$	657	668	685	666	664	671	675
CH$_2$=NHCH$_3$$^+$	695	706	726	708	706	714	723
CH$_3$CH$_2$CH=NH$_2$$^+$ [f]	636	652[g]	661	636	631	640	643
(CH$_3$)$_2$C=NH$_2$$^+$	590	608[g]	616	593	588	595	599
E-CH$_3$CH=NHCH$_3$$^+$	615	631	657	633	629	638	645
Z-CH$_3$CH=NHCH$_3$$^+$			664	640	636	645	653
CH$_2$=NHCH$_2$CH$_3$$^+$ [h]	653	666	695	670	667	676	684
CH$_2$=N(CH$_3$)$_2$$^+$	661	676	694	669	666	675	688
CH$_3$CH$_2$CH$_2$CH=NH$_2$$^+$ [i]			643	612	605	614	616
(CH$_3$)$_2$CHCH=NH$_2$$^+$			635	604	597	607	611
CH$_3$CH$_2$(CH$_3$)C=NH$_2$$^+$			594	564	557	564	570
E-CH$_3$CH$_2$CH=NHCH$_3$$^+$ [j]			635	604	598	608	614
Z-CH$_3$CH$_2$CH=NHCH$_3$$^+$			646	616	610	620	627
(CH$_3$)$_2$C=NHCH$_3$$^+$			601	571	565	574	581
E-CH$_3$CH=NHCH$_2$CH$_3$$^+$	615[k]		627	597	591	601	607
Z-CH$_3$CH=NHCH$_2$CH$_3$$^+$			635	605	598	609	616
CH$_2$=NHCH$_2$CH$_2$CH$_3$$^+$ [l]			677	646	640	649	657
CH$_2$=NHCH(CH$_3$)$_2$$^+$			659	628	622	633	637
CH$_3$CH=N(CH$_3$)$_2$$^+$	640[k]		639	610	604	614	625
CH$_2$=N(CH$_3$)C$_2$H$_5$$^+$			666	635	630	641	652
CH$_3$CH$_2$CH$_2$CH$_2$CH=NH$_2$$^+$			626	590	580	586	591
CH$_3$CH$_2$CH$_2$(CH$_3$)C=NH$_2$$^+$			577	541	532	533	542
CH$_3$CH$_2$(CH$_3$)CHCH=NH$_2$$^+$			617	581	572	580	584
E-CH$_3$CH$_2$CH$_2$CH=NHCH$_3$$^+$ [m]			617	581	572	582	587
E-CH$_3$CH$_2$(CH$_3$)C=NHCH$_3$$^+$			579	543	535	541	550
(CH$_3$)$_2$C=NHCH$_2$CH$_3$$^+$			572	537	528	538	545
E-CH$_3$CH=NHCH$_2$CH$_2$CH$_3$$^+$			609	573	565	574	580
E-CH$_3$CH=NHCH(CH$_3$)$_2$$^+$			592	556	549	559	562
CH$_2$=NHCH$_2$CH$_2$CH$_2$CH$_3$$^+$			660	623	615	624	633
CH$_2$=NHCH(CH$_3$)CH$_2$CH$_3$$^+$			639	602	593	605	610
(CH$_3$)$_2$C=N(CH$_3$)$_2$$^+$			593	558	550	560	569
CH$_2$=N(CH$_3$)CH$_2$CH$_2$CH$_3$$^+$			647	611	603	614	626
CH$_2$=N(CH$_3$)CH(CH$_3$)$_2$$^+$			634	597	589	601	609
CH$_2$=N(CH$_2$CH$_3$)$_2$$^+$			638	601	593	606	616

[a] Heats of formation in kJ mol^{-1}. The same $\Delta H_{f,298}^\circ$ − $\Delta H_{f,0}^\circ$ difference was obtained for all four methods. [b] 298 K heats of formation taken from ref 5 unless otherwise indicated. [c] Rederived heats of formation, using the experimentally determined appearance energies (ref 5) and Traeger and McLoughlin's 298 K enthalpy contributions (ref 38). The auxiliary thermochemistry is given in Table 5. [d] The G2(MP2) heats of formation differ slightly from the values reported in ref 14, owing to differences between vibrational frequencies calculated at the HF/6-31G(d) and HF/6-31G(d,p) levels. [e] Dyke (ref 45) reports 755 kJ mol^{-1}. [f] NCCC dihedral angle of 0°; $\Delta H_{f,298}^\circ$ of the conformer with an NCCC angle of 120° is 641, 645 kJ mol^{-1} [G2(MP2), CBS-Q]. [g] Value presumed to be high owing to barrier to the reverse reaction (see text). [h] CNCC dihedral angle of 120°; $\Delta H_{f,298}^\circ$ of the conformer with an NCCC angle of 0° is 671, 677 kJ mol^{-1} [G2(MP2), CBS-Q]. [i] NCCC dihedral angle of 0°; $\Delta H_{f,298}^\circ$ of the conformer with an NCCC angle of 120° is 615, 618 kJ mol^{-1} [G2(MP2), CBS-Q]. [j] NCCC dihedral angle of 0°; $\Delta H_{f,298}^\circ$ of the conformer with an NCCC angle of 120° is 609, 613 kJ mol^{-1} [G2(MP2), CBS-Q]. [k] From ref 19. [l] CNCC dihedral angle of 120°; $\Delta H_{f,298}^\circ$ of the conformer with an NCCC angle of 0° is 648, 651 kJ mol^{-1} [G2(MP2), CBS-Q]. [m] NCCC dihedral angle of 0°; $\Delta H_{f,298}^\circ$ of the conformer with an NCCC angle of 120° is 584, 586 kJ mol^{-1} [G2(MP2), CBS-Q].

kJ mol^{-1}), but it is slightly lower when longer-chain substituents are present (e.g., CH$_3$CH$_2$CH$_2$CH=NH$_2$$^+$ and CH$_3$CH$_2$CH$_2$-CH=NHCH$_3$$^+$, 3 kJ mol^{-1}). The preference is reversed for alkyl chains on the N-terminus of the immonium ion, in that the more stable conformer has hydrogen rather than carbon eclipsing the N=C group (CCNC dihedral angle close to 120°; Figure 2b). The difference in energy depends on whether the nitrogen is protonated; it is considerably lower for N-alkyl immonium ions

than for N-substituted imines (see above), e.g., for CH$_2$=NHCH$_2$-CH$_3$$^+$ and CH$_2$=NHCH$_2$CH$_2$CH$_3$$^+$, we find energy differences of between 1 and 2 kJ mol^{-1} between the eclipsed conformers.

The presence of secondary alkyl groups on C or N (Figure 3) will, in many cases, give rise to gauche interactions. Our calculations for immonium ions in various conformations show that gauche−anti energy differences amount to about 4 kJ mol^{-1} when two methyl groups are involved, in good agreement with

Table 5. Auxiliary Thermochemistry[a]

	$\Delta H^\circ_{f,298}$		$\Delta H^\circ_{f,298}$
H•	218[b]	CH₃NH₂	−23
CH₃•	147[c]	CH₃CH₂NH₂	−47
C₂H₅•	119[c]	CH₃NHCH₃	−19
•CH₂OH	−18[d]	CH₃CH₂CH₂NH₂	−70
		(CH₃)₂CHNH₂	−84
HOCH₂CH₂NH₂	−202	CH₃CH₂NHCH₃	−46[b]
HOCH₂CH(CH₃)NH₂	−238	(CH₃)₃N	−24
HOCH₂CH₂NHCH₃	−200	C₂H₅(CH₃)CHNH₂	−105
HOCH₂(CH₃)₂CNH₂	−272	(CH₃)₃CNH₂	−121
HOCH₂CH₂N(CH₃)₂	−204	CH₃CH₂NHCH₂CH₃	−73
HOCH₂CH₂NHCH₂CH₃	−227	(CH₃)₂CHNHCH₃	−84[e]
HOCH₂CH(C₂H₅)NH₂	−259	(CH₃)₂NCH₂CH₃	−48[b]

[a] Values in kJ mol⁻¹; unless otherwise indicated, the heats of formation of neutral amines are taken from ref 31 and additivity estimates of the heats of formation of amino alcohols from ref 5. The integrated heat capacities calculated [based on scaled HF/6-31G(d) frequencies] for CH₃•, C₂H₅•, and •CH₂OH are 11, 13, and 11 kJ mol⁻¹, respectively. [b] From ref 19. [c] From ref 46. [d] From ref 47. [e] From ref 5.

Table 6. Group Additivity Values for Immonium Ions[a]

N$_{imo}$H₂	710.5	C$_{imo}$H₂	26.2[b]
N$_{imo}$−(C,H)	721.1	C$_{imo}$−(C,H)	−4.2
N$_{imo}$−(2C)	728.7	C$_{imo}$−(2C)	−33.3
CH₂−(N$_{imo}$,C)	−35.5	CH₂−(C$_{imo}$,C)	−29.0
CH−(N$_{imo}$,2C)	−35.9	CH−(C$_{imo}$,2C)	−18.3
CH₃−(N$_{imo}$)	−41.8[c]	CH₃−(C$_{imo}$)	−41.8[c]
CH₃−(C)	−41.8[c]	CH₂−(2C)	−20.9[c]
cis correction[d]	8.8	γ correction (N-subst.)	−4.2
γ correction (C-subst)[e]	−2.7		

[a] Values in kJ mol⁻¹. [b] Assigned to be equal to Benson's value (ref 27) for C₄H₂. [c] Assigned (ref 27). [d] The cis correction applies when two alkyl groups on the C=N double bond are cis with respect to each other. [e] The γ corrections are applied when the immonium ion substituents on C, respectively, N include γ-carbon atoms.

many experimental results.[41] Gauche interactions involving the −CH=NH₂⁺ or −NH=CH₂⁺ groups appear not to give rise to substantial energy differences.

Group Additivity Values for Immonium Ions. Additivity methods are not in common use for assessing the heats of formation of ionic species. Cohen and Benson[41] have pointed out, using polyfluoroalkanes as an example, that molecules with strongly polarizing groups may exhibit significant deviations from additivity, and the presence of a charge could be expected to have similar consequences. Furthermore, it has been argued[19] that simple additivity schemes cannot be expected to work well for ions because the ionization energies for homologous series do not exhibit a linear dependence on molecular size; whether this argument would apply to the heats of formation of even-electron ions is not clear. However, we find that the G2(MP2) heats of formation of immonium ions are well reproduced by a Benson additivity scheme. To derive the group additivity values in Table 6, we have included results for 14 C₅-immonium ions, to ensure that each group is represented several times in the data. The resulting set of additivity values includes two correction terms for non-nearest-neighbor interactions, namely a cis correction that applies whenever two alkyl substituents are cis with respect to the C=N double bond and a γ correction that accounts for the additional charge-induced dipole stabilization of the immonium ion brought about by alkyl groups longer than ethyl. The γ correction is different for *C*- and *N*-alkyl groups but is, in both cases, small, −2.6 and −4.2 kJ mol⁻¹, respectively. The set does not include a gauche correction, since

Figure 2. Preferred eclipsed conformations of immonium ions. (a) Methyl group in C=N plane; (b) H in C=N plane.
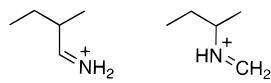
Figure 3.

only one of the immonium ions examined in this study will necessarily have gauche CH₃/CH₃ interactions.

We have chosen to assign the conventional additivity value for methyl groups also to the CH₃ groups that are bonded directly to the C=N⁺ group and to take the value for an immonium ion =CH₂ group, C$_{imo}$H₂, to be the same as that for =CH₂ in imines, that is, the value for a terminal alkene =CH₂. It may appear questionable to perform an assignment by analogy to a component of the formally charge-carrying part of the immonium ion, but some assignments are by nature arbitrary and should, as far as possible, be chosen to yield group additivity values that are consistent and comparable across compound classes. Other assignments for C$_{imo}$H₂ (or another of the C=N parameters) would be possible, but all valid assignments result in equivalent sets of group additivity values, which yield the same predictions for the heats of formation.

Of the 35 immonium ions included in the present study, three were not included in the derivation of the group additivity values because unfavorable steric interactions in these ions would require the introduction of additional correction terms: the *N*-methyl group in Z-CH₃NH=CHCH₂CH₃⁺ prevents the terminal methyl group from occupying the otherwise favored eclipsing position, CH₂=N(CH₃)CH(CH₃)₂⁺ exhibits gauche-type interactions, and the double cis interactions in (CH₃)₂-N=C(CH₃)₂⁺ require additional corrections, as do tetrasubstituted ethylenes.[26] The heat of formation of the smallest immonium ion, CH₂=NH₂⁺, is not well reproduced by our additivity scheme, and results for this ion were not included in the derivation of the immonium ion group additivity values in Table 6. Preliminary studies of additivity schemes for oxonium ions indicate similar deviations for the first member of the series.[42]

The additivity scheme reproduces the G2(MP2) heats of formation to within 2 kJ mol⁻¹ for the 31 immonium ions used to derive the group additivity values (Table 7), and the values for the three compounds not included in the derivation for stereochemical reasons are off by only 3 kJ mol⁻¹. This suggests that our group additivity values can be used with confidence to estimate the heats of formation of immonium ions without severe steric congestion.

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Table 7. Heats of Formation of Immonium Ions Estimated by Additivity[a]

	add[b]	diff[c]		add[b]	diff[c]		add[b]	diff[c]
$CH_2=NH_2^{+\ d}$	737	−12	$E\text{-}CH_3CH_2CH=NHCH_3^+$	604	0	$E\text{-}CH_3CH_2CH_2CH=NHCH_3^+$	581	0
$CH_3CH=NH_2^+$	664	−2	$Z\text{-}CH_3CH_2CH=NHCH_3^{+\ d}$	613	−3	$E\text{-}CH_3CH_2(CH_3)C=NHCH_3^+$	542	−1
$CH_2=NHCH_3^+$	706	−2	$(CH_3)_2C=NHCH_3^+$	571	0	$(CH_3)_2C=NHCH_2CH_3^+$	536	−1
$CH_3CH_2CH=NH_2^+$	636	−1	$E\text{-}CH_3CH=NHCH_2CH_3^+$	598	1	$E\text{-}CH_3CH=NHCH_2CH_2CH_3^+$	573	0
$(CH_3)_2C=NH_2^+$	594	1	$Z\text{-}CH_3CH=NHCH_2CH_3^+$	607	2	$E\text{-}CH_3CH=NHCH(CH_3)_2^+$	556	0
$E\text{-}CH_3CH=NHCH_3^+$	633	0	$CH_2=NHCH_2CH_2CH_3^+$	645	−1	$CH_2=NHCH_2CH_2CH_2CH_3^+$	624	1
$Z\text{-}CH_3CH=NHCH_3^+$	642	2	$CH_2=NHCH(CH_3)_2^+$	628	0	$CH_2=NHCH(CH_3)CH_2CH_3^+$	603	1
$CH_2=NHCH_2CH_3^+$	670	0	$CH_3CH=N(CH_3)_2^+$	608	−2	$(CH_3)_2C=N(CH_3)_2^{+\ d}$	555[e]	−3
$CH_2=N(CH_3)_2^+$	671	2	$CH_2=N(CH_3)CH_2CH_3^+$	636	1	$CH_2=N(CH_3)CH_2CH_2CH_3^+$	611	0
$CH_3CH_2CH_2CH=NH_2^+$	612	0	$CH_3CH_2CH_2CH_2CH=NH_2^+$	591	1	$CH_2=N(CH_3)CH(CH_3)_2^{+\ d}$	594	−3
$(CH_3)_2CHCH=NH_2^+$	604	0	$CH_3CH_2CH_2(CH_3)C=NH_2^+$	541	0	$CH_2=N(CH_2CH_3)_2^+$	600	−1
$CH_3CH_2(CH_3)C=NH_2^+$	565	1	$CH_3CH_2(CH_3)CHCH=NH_2^+$	581	0			

[a] Values in kJ mol^{-1}; group additivity values in Table 6. [b] Value calculated by additivity. [c] $\Delta H_f^\circ[\text{additivity}] - \Delta H_f^\circ[\text{G2(MP2)}]$. [d] Ion not included in the derivation of group additivity values; reasons given in the text. [e] Cis interactions treated as for tetrasubstituted ethylenes (ref 26), i.e., three cis corrections applied.

Table 8. Proton Affinities of C_1–C_4 Aliphatic Imines[a]

	exp	G2(MP2)	G2(MP2, SVP)	CBS-Q	CBS-q
$CH_2=NH$	860[b]	869[c]	867	868	871
$E\text{-}CH_3CH=NH$	897[d]	907	906	907	909
$Z\text{-}CH_3CH=NH$		910	909	910	912
$CH_2=NCH_3$	880[d]	902	901	900	901
$E\text{-}CH_3CH_2CH=NH$		918	917	918	920
$Z\text{-}CH_3CH_2CH=NH$		923	922	922	924
$(CH_3)_2C=NH$	934[e]	940	939	941	937
$E\text{-}CH_3CH=NCH_3$		934	933	932	933
$Z\text{-}CH_3CH=NCH_3$		943	942	942	943
$CH_2=NCH_2CH_3$		913	912	912	912
$E\text{-}CH_3CH_2CH_2CH=NH$		923	922	923	926
$Z\text{-}CH_3CH_2CH_2CH=NH$		926	925	926	929
$E\text{-}(CH_3)_2CHCH=NH$		924	923	923	925
$Z\text{-}(CH_3)_2CHCH=NH$		927	926	926	927
$E\text{-}CH_3CH_2(CH_3)C=NH$		949	948	950	947
$Z\text{-}CH_3CH_2(CH_3)C=NH$		950	949	950	947
$E\text{-}CH_3CH_2CH=NCH_3$		944	943	942	944
$Z\text{-}CH_3CH_2CH=NCH_3$		950	949	948	950
$(CH_3)_2C=NCH_3$		968	967	967	965
$E\text{-}CH_3CH=NCH_2CH_3$	936[f]	943	942	942	943
$Z\text{-}CH_3CH=NCH_2CH_3$		952	951	951	952
$CH_2=NCH_2CH_2CH_3$		917	916	918	917
$CH_2=NCH(CH_3)_2$		922	921	920	920

[a] Proton affinities in kJ mol^{-1}. [b] From ref 4. [c] Suarez and Sordo (ref 48) report 867 kJ mol^{-1}, obtained by calculation at the QCISD(T)/6-311+G(3df,2p) level. [d] From ref 3. [e] From ref 49. [f] From ref 1.

Proton Affinities of Imines. The four composite methods yield proton affinities of the C_1–C_4 aliphatic imines (Table 8) that are, in most cases, within 2 kJ mol^{-1} of each other. The differences between the results obtained with the four methods are much less pronounced for the proton affinities of imines than for the heats of formation of the imines and immonium ions, presumably because the use of eq 5 to determine proton affinities allows for significant error compensation. Only five experimentally determined proton affinities of C_1–C_4 imines are available (Table 8); the agreement between experiment and calculation is reasonable, with the exception of PA-($CH_2=NCH_3$).

For amines, the increase in proton affinity caused by the introduction of alkyl substituents on the nitrogen atom is considerably more pronounced than that caused by substituents on the α-carbon.[1] The reverse situation obtains for imines, PA-($CH_3CH=NH$) being some 6 kJ mol^{-1} higher than PA-($CH_2=NCH_3$). This reflects that alkyl substituents on carbon stabilize the immonium ion more than do alkyl substituents on nitrogen. We note also that cis imines are more basic than trans imines, e.g. the proton affinity of *cis*-$CH_3CH=NCH_3$ is 9 kJ mol^{-1} higher than that of the trans form, illustrating that the cis/trans energy difference is considerably larger for imines than for immonium ions.

To associate proton affinity and hybridization on N may well be less useful than assumed by previous authors. The proton affinity of CH_3NH_2 is some 30 kJ mol^{-1} higher than that of $CH_2=NH$, possibly indicating that the sp^2-hybridized nitrogen is less basic than sp^3-hybridized nitrogen. However, the proton affinity difference between $CH_3CH=NH$ and $CH_3CH_2NH_2$ is less than 10 kJ mol^{-1}, which could be taken to indicate that there is only little difference between the basicity of sp^2 and sp^3 nitrogen, and the proton affinity of $(CH_3)_2C=NH$ is some 15 kJ mol^{-1} higher than that of $(CH_3)_2CHNH_2$, which would perhaps suggest that the sp^2 nitrogen is the more basic. These variations arise because the proton affinity reflects the properties of the acid−base pair under consideration, not just the properties of the base. It would appear that, in the present system, hybridization effects are less important than the effects that influence the stabilization of charge on the immonium ion carbon atom.

Conclusions

The agreement obtained between the heats of formation and proton affinities calculated with ab initio methods and the values derived from experimental measurements suggests that the computational results are sufficiently accurate to be useful in studies of the formation and reactions of imines and immonium ions in the gas phase. The results emphasize that 298 K enthalpy contributions such as those proposed by Traeger and McLoughlin[38] should be included when heats of formation are derived from threshold energy measurements. The reported appearance energies[5] for the formation of $(CH_3)_2C=NH_2^+$ and $CH_3CH_2CH=NH_2^+$ appear to be higher than the thermochemical threshold, which supports previous evidence to indicate the presence of energy barriers in excess of the reaction endothermicity for simple α-cleavage in some systems.[39]

The CBS-Q heats of formation of small imines and immonium ions are consistently higher than the G2(MP2) values, but the available experimental data are not sufficiently accurate to indicate if one method is to be preferred over the other. Practical considerations would suggest the use of the CBS-Q method, as this is somewhat more economical in terms of computer resources. The differences between the G2(MP2,SVP) heats of formation and those obtained with the G2(MP2) or CBS-Q methods for imines and immonium ions increase with the size of the molecule, suggesting that G2(MP2,SVP) results for larger systems should be used with caution (and possibly with adjustment, since the deviations appear to be systematic). The CBS-q results also differ from the G2(MP2) and CBS-Q results

in a somewhat systematic fashion, but neither this method nor CBS-4 appears well suited for studies of the present systems. Despite these shortcomings, the proton affinity calculations with the G2(MP2,SVP) and CBS-q methods yield almost the same results as do calculations with the G2(MP2) and CBS-Q methods, indicating error compensation to a considerable extent.

Stereochemical and conformational factors influence the heats of formation of imines and immonium ions significantly. The lower-energy conformations of imines and immonium ions with ethyl or longer alkyl groups are eclipsed; in *C*-alkyl substituents the β-carbon eclipses the C=N group, whereas the eclipsing atom in *N*-alkyl groups is a hydrogen. The energy difference between the eclipsed conformers depends on whether the nitrogen is protonated; the difference is particularly large for *N*-alkyl imines (7−8 kJ mol^{-1}). Also, the cis/trans energy difference is more pronounced for imines than for immonium ions (16−17 kJ mol^{-1}); the reasons for this are not clear.

The additivity scheme established to determine heats of formation for immonium ions reproduces the ab initio results well, but we do not expect that the present scheme will provide quite the same degree of accuracy as Benson-type additivity methods do when used for neutral molecules.

Supporting Information Available: Calculated total enegies obtained with the G2(MP2), G2(MP2,SVP), CBS-Q, and CBS-q methods, and integrated heat capacities derived from scaled HF/6-31G(d) frequencies of imines (Table S1) and immonium ions (Table S2) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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