International Journal of Mass Spectrometry 179/180 (1998) 301–308

Heats of formation of imine and enamine radical cations and the corresponding neutral molecules

Jens Henriksen, Steen Hammerum*

Department of Chemistry, The University of Copenhagen, The H.C. Ørsted Institute, DK-2100 Copenhagen Ø, Denmark

Received 11 May 1998; accepted 15 July 1998

Abstract

The heats of formation of imines and enamines with up to four carbon atoms were determined with the CBS-Q and G2 (MP2) composite high-level ab initio procedures. The imines are lower in energy than the corresponding enamines; the energy difference is typically some 15 kJ mol^{-1}, which is considerably less than that observed for isomeric keto–enol pairs. *N*-alkyl enamines are more stable as the *syn* form, by approximately 7 kJ mol^{-1}. The heats of formation of enamine radical cations are between 80 and 170 kJ mol^{-1} lower than the heats of formation of their imine counterparts, depending on the presence of substituents on the double bond and the nitrogen atom. (Int J Mass Spectrom 179/180 (1998) 301–308) © 1998 Elsevier Science B.V.

Keywords: Heats of formation; Imines; Enamines; Ab initio calculations; G2(MP2); CBS-Q

1. Introduction

It is well established that neutral ketones and aldehydes have lower heats of formation than the corresponding enols, whereas the reverse relationship is obtained for the radical cations [1–3]; this phenomenon was called a “stability inversion” by Haselbach [4]. The nitrogen analogs, imines, and enamines, have not been as widely studied. The few results available in the literature with regard to their heats of formation indicate that imine–enamine pairs and the corresponding radical cations obey a similar relationship [4–9], but a systematic study is not available. To remedy this situation we have undertaken a computational investigation of the thermochemistry of neutral and ionized imines and enamines. Direct, experimental studies of these systems are in many cases not practical, inasmuch as simple imines and enamines readily undergo condensation and polymerization reactions [10]. However, with the introduction of high-level composite ab initio methods in computational chemistry it has become possible on a routine basis to calculate the thermochemical properties of small molecules and ions with an accuracy comparable to that of most experimental determinations [11–15]. In an attempt to strike a compromise between accuracy and computational expense we have chosen the G2(MP2) and CBS-Q methods from Pople’s G2 family and Petersson’s CBS family of composite ab initio methods for the present study of the heats of formation of all imine and enamine neutral molecules and radical cations with up to four carbon atoms.

---

* Corresponding author. E-mail: steen@kiku.dk

Dedicated to Professor Fulvio Cacace in recognition of his many contributions to gas-phase and condensed-phase ion chemistry.

PII S1387-3806(98)14145-3

Table 1
Calculated total energies of C_2–C_4 enamines[a]

	G2(MP2)	CBS-Q
$CH_2=CHNH_2$	−133.688 22	−133.692 77
E-$CH_3CH=CHNH_2$	−172.914 08	−172.920 08
Z-$CH_3CH=CHNH_2$	−172.914 50	−172.920 11
$CH_2=C(CH_3)NH_2$	−172.919 71	−172.925 25
syn-$CH_2=CHNHCH_3$	−172.904 97	−172.910 27
anti-$CH_2=CHNHCH_3$	−172.902 45	−172.907 76
E-$CH_3CH_2CH=CHNH_2$	−212.138 53	−212.145 80
Z-$CH_3CH_2CH=CHNH_2$	−212.138 86	−212.145 44
$(CH_3)_2C=CHNH_2$	−212.143 00	−212.149 91
E-$CH_3CH=C(CH_3)NH_2$	−212.143 45	−212.151 14
Z-$CH_3CH=C(CH_3)NH_2$	−212.146 19	−212.154 05
$CH_2=C(CH_2CH_3)NH_2$	−212.143 42	−212.149 92
E, *syn*-$CH_3CH=CHNHCH_3$	−212.130 63	−212.137 56
E, *anti*-$CH_3CH=CHNHCH_3$	−212.128 51	−212.135 49
Z, *syn*-$CH_3CH=CHNHCH_3$	−212.123 99	−212.130 47
Z, *anti*-$CH_3CH=CHNHCH_3$	−212.128 79	−212.135 27
anti-$CH_2=C(CH_3)NHCH_3$	−212.132 23	−212.139 41
syn-$CH_2=C(CH_3)NHCH_3$	−212.136 39	−212.143 09
$CH_2=CHN(CH_3)_2$	−212.122 84	−212.129 10
anti-$CH_2=CHNHCH_2CH_3$	−212.129 97	−212.136 26
syn-$CH_2=CHNHCH_2CH_3$	−212.132 01	−212.138 64

[a] Hartrees.

2. Methods

The CBS-Q [14] and G2(MP2) [12] energies of imine and enamine molecules and radical cations were calculated with the GAUSSIAN-94 suite of programs [16]. The 0 and 298 K heats of formation were derived from the calculated electronic energies and vibrational frequencies as described by Nicolaides et al. [17]; the required experimentally determined enthalpies and heats of formation of atoms were taken from the 1982 NBS compilation by Wagman et al. [18].

The calculated total energies of imine radical cations and enamine molecules and radical cations are given in Tables 1–3; the energies of neutral imines are reported elsewhere [19]. The derived heats of formation are given in Tables 4 and 5 and typical geometric properties in Table 6.

The heats of formation of imine and enamine radical cations derived from the CBS-Q energies turn out to be some 5 kJ mol^{-1} lower than those derived from G2(MP2) energies. This contrasts with the trend observed for other classes of compound [15,19], in that the CBS-Q heats of formation are often higher than the G2(MP2) values. The CBS-Q heats of formation of neutral enamines are uniformly slightly higher (~2 kJ mol^{-1}) than those derived from G2(MP2) calculations.

Very few well-determined experimental values are available in the literature for the species included in the present study. For vinylamine, our calculated heat of formation is some 40 kJ mol^{-1} higher than the literature value [9], and 25 kJ mol^{-1} higher than the estimate by Bouchoux et al. [6]; this discrepancy was already noted by Smith and Radom [20]. The heat of formation of propenylamine was estimated by Bouchoux et al. [21] to be 30 kJ mol^{-1}, in reasonable agreement with our results. For the vinylamine radical cation our calculated value is close to that determined experimentally by Bouchoux et al. [22], and our value for the propenylamine radical cation is, likewise, not very different from that estimated by Bouchoux [21]. Our calculated ΔH_f of $CH_2 = NH^{+\cdot}$ agrees well with that derived by Holmes [23] from experimental measurements and with the results of previous calculations [24].

Table 2
Calculated total energies of C_2–C_4 enamine radical cations[a]

	G2(MP2)	CBS-Q	$\langle S^2\rangle$[b]
$\mathrm{CH_2{=}CHNH_2^{+\cdot}}$	−133.387 55	−133.394 09	0.823
E-$\mathrm{CH_3CH{=}CHNH_2^{+\cdot}}$	−172.628 59	−172.637 17	0.808
Z-$\mathrm{CH_3CH{=}CHNH_2^{+\cdot}}$	−172.627 31	−172.635 37	0.805
$\mathrm{CH_2{=}C(CH_3)NH_2^{+\cdot}}$	−172.630 05	−172.638 08	0.797
syn-$\mathrm{CH_2{=}CHNHCH_{3+}^{\cdot}}$	−172.616 35	−172.624 12	0.861
anti-$\mathrm{CH_2{=}CHNHCH_3^{+\cdot}}$	−172.618 43	−172.626 42	0.866
E-$\mathrm{CH_3CH_2CH{=}CHNH_2^{+\cdot}}$	−211.854 61	−211.864 57	0.806
Z-$\mathrm{CH_3CH_2CH{=}CHNH_2^{+\cdot}}$	−211.853 46	−211.862 56	0.804
$\mathrm{(CH_3)_2C{=}CHNH_2^{+\cdot}}$	−211.867 68	−211.877 28	0.790
E-$\mathrm{CH_3CH{=}C(CH_3)NH_2^{+\cdot}}$	−211.868 76	−211.879 06	0.793
Z-$\mathrm{CH_3CH{=}C(CH_3)NH_2^{+\cdot}}$	−211.868 20	−211.878 22	0.785
$\mathrm{CH_2{=}C(CH_2CH_3)NH_2^{+\cdot}}$	−211.856 65	−211.866 17	0.796
E, syn-$\mathrm{CH_3CH{=}CHNHCH_3^{+\cdot}}$	−211.855 97	−211.865 97	0.842
E, anti-$\mathrm{CH_3CH{=}CHNHCH_3^{+\cdot}}$	−211.857 65	−211.867 92	0.847
Z, syn-$\mathrm{CH_3CH{=}CHNHCH_3^{+\cdot}}$	−211.849 63	−211.859 19	0.840
Z, anti-$\mathrm{CH_3CH{=}CHNHCH_3^{+\cdot}}$	−211.856 31	−211.866 08	0.843
anti-$\mathrm{CH_2{=}C(CH_3)NHCH_3^{+\cdot}}$	−211.857 21	−211.866 96	0.840
syn-$\mathrm{CH_2{=}C(CH_3)NHCH_3^{+\cdot}}$	−211.856 55	−211.865 74	0.827
$\mathrm{CH_2{=}CHN(CH_3)_2^{+\cdot}}$	−211.846 75	−211.856 05	0.902
anti-$\mathrm{CH_2{=}CHNHCH_2CH_3^{+\cdot}}$	−211.849 13	−211.858 43	0.870
syn-$\mathrm{CH_2{=}CHNHCH_2CH_3^{+\cdot}}$	−211.846 96	−211.856 02	0.866

[a] Hartrees.
[b] QCISD(T)/6-311G(d,p).

Spin contamination can be a problem when unrestricted wave functions are used in studies of open-shell systems. Tables 2 and 3 include the $\langle S^2\rangle$ expectation values of the QCISD(T) step of the G2(MP2) procedure; the other post-Hartree–Fock steps of the G2(MP2) and CBS-Q methods yield almost identical values. The possible error arising from the moderate spin contamination encountered will not significantly influence the energy differences between imine and enamine radical cations.

3. Results and discussion

3.1. Neutral enamines

The calculated heats of formation of enamine molecules (Table 4) show a number of systematic trends: The introduction of methyl groups on the nitrogen atom does not influence the heat of formation very much; the values for vinylamine and its *N*-methyl and *N*,*N*-dimethyl homologs are within 10 kJ of each other (Table 4). In this, the enamines resemble saturated aliphatic amines, e.g., the heats of formation of methyl-, dimethyl- and trimethylamine are −23, −19, and −24 kJ $\mathrm{mol^{-1}}$, respectively. The introduction of methyl groups on the α-carbon atom of the CC double bond lowers the heat of formation by 35–40 kJ $\mathrm{mol^{-1}}$; a methyl group on the β-carbon atom lowers ΔH_f by some 25 kJ $\mathrm{mol^{-1}}$.

The heats of formation of *cis/trans* isomeric enamines differ very little when the amino group is involved, e.g. the *Z* and *E* forms of 1-propenylamine (Fig. 1) have almost the same heat of formation. Turecek and Cramer [2] reported similar results with regard to the relative stability of *cis/trans* isomeric enols. However, substantial differences are encountered when the geometrical isomerism involves two methyl groups, viz. the energy difference between the two 2-buten-2-ylamines (Fig. 1) is even higher than the difference between the *cis*- and *trans*-2-butenes.

Conversely, the heats of formation of *syn* and *anti* isomeric *N*-substituted enamines are appreciably dif-

Table 3
Calculated total energies of C_1–C_4 imine radical cations[a]

	G2(MP2)	CBS-Q	$\langle S^2\rangle$[b]
$CH_2{=}NH^{+\cdot}$	−94.093 84	−94.098 94	0.845
E-$CH_3CH{=}NH^{+\cdot}$	−133.342 20	−133.348 44	0.815
Z-$CH_3CH{=}NH^{+\cdot}$	−133.341 97	−133.348 17	0.816
$CH_2{=}NCH_3^{+\cdot}$	−133.343 21	−133.349 83	0.872
E-$CH_3CH_2CH{=}NH^{+\cdot}$	−172.570 92	−172.578 16	0.811
Z-$CH_3CH_2CH{=}NH^{+\cdot}$	−172.571 22	−172.578 45	0.812
$(CH_3)_2C{=}NH^{+\cdot}$	−172.588 07	−172.596 01	0.799
E-$CH_3CH{=}NCH_3^{+\cdot}$	−172.587 74	−172.595 99	0.840
Z-$CH_3CH{=}NCH_3^{+\cdot}$	−172.587 61	−172.595 58	0.841
$CH_2{=}NCH_2CH_3^{+\cdot}$	−172.576 26	−172.584 10	0.873
E-$CH_3CH_2CH_2CH{=}NH^{+\cdot}$	−211.797 56	−211.806 52	0.811
Z-$CH_3CH_2CH_2CH{=}NH^{+\cdot}$	−211.798 38	−211.807 43	0.812
E-$(CH_3)_2CHCH{=}NH^{+\cdot}$	−211.802 05	−211.810 56	0.809
Z-$(CH_3)_2CHCH{=}NH^{+\cdot}$	−211.803 71	−211.812 21	0.810
E-$CH_3CH_2C(CH_3){=}NH^{+\cdot}$	−211.816 07	−211.825 14	0.797
Z-$CH_3CH_2C(CH_3){=}NH^{+\cdot}$	−211.816 44	−211.825 46	0.798
E-$CH_3CH_2CH{=}NCH_3^{+\cdot}$	−211.815 58	−211.825 19	0.835
Z-$CH_3CH_2CH{=}NCH_3^{+\cdot}$	−211.815 65	−211.824 34	0.838
$(CH_3)_2C{=}NCH_3^{+\cdot}$	−211.830 73	−211.840 30	0.820
E-$CH_3CH{=}NCH_2CH_3^{+\cdot}$	−211.820 15	−211.829 66	0.843
Z-$CH_3CH{=}NCH_2CH_3^{+\cdot}$	−211.818 86	−211.828 27	0.842
$CH_2{=}NCH_2CH_2CH_3^{+\cdot}$	−211.804 45	−211.813 91	0.874
$CH_2{=}NCH(CH_3)_2^{+\cdot}$	−211.809 90	−211.819 33	0.874

[a] Hartrees.
[b] QCISD(T)/6-311G(d,p).

ferent, the *syn* isomer being the more stable by on average 7 kJ mol^{-1}; this agrees well with the situation observed for enol ethers [25]. The *N*-alkyl group in the *syn* isomer does not quite eclipse the double bond, e.g., for the two isomers of *N*-methylvinylamine (Fig. 1) we find dihedral CNCC angles of ~15° and ~145°. The barrier to interconversion of the *syn* and *anti* isomers by rotation around the central C–N bond is calculated to be 27 kJ mol^{-1} (CBS-Q 298 K energy difference between the *syn* form and the transition state for interconversion). Interconversion of the *E* and *Z* forms of 1-propenylamine by rotation around the C ═ C double bond would require approximately 260 kJ mol^{-1}.

3.2. Enamine radical cations

The introduction of a methyl group on either carbon atom of the double bond lowers the heat of formation by approximately 65 kJ mol^{-1} (Table 4), whereas a methyl substituent on the nitrogen lowers the heat of formation by some 35 kJ mol^{-1}. The effect of additional methyl groups is slightly less pronounced, 60 kJ mol^{-1}, respectively, 30 kJ mol^{-1}.

The heats of formation of *cis/trans* isomers and *syn/anti* isomers of enamine radical cations differ by about 5 kJ mol^{-1}, the *trans* and *anti* forms being the more stable. In this the properties of the enamine radical cations differ from those of the neutral enamines described above and to some extent from those observed for enol radical cations; for the latter Turecek and Cramer's results [2] show that the heats of formation of *cis* and *trans* isomers are almost the same (in preliminary studies, we find that this applies to enol ether radical cations as well).

The barrier to rotation around the central C–N bond in the *N*-methylvinylamine radical cation is 108 kJ mol^{-1} (CBS-Q 298 K energy difference between the *anti* form and the transition state for interconversion), considerably higher than that found for the

Table 4
Calculated heats of formation of C_2–C_4 enamines and the corresponding radical cations[a]

	Neutral enamines			Radical cations		
	G2(MP2)		CBS-Q[b]	G2(MP2)		CBS-Q[b]
	0 K	298 K	298 K	0 K	298 K	298 K
$CH_2{=}CHNH_2$	74	60	62	864	849	846
E-$CH_3CH{=}CHNH_2$	57	37	38	807	786	780
Z-$CH_3CH{=}CHNH_2$	56	36	38	810	790	785
$CH_2{=}C(CH_3)NH_2$	42	21	24	803	782	778
syn-$CH_2{=}CHNHCH_3$	81	60	63	839	818	815
anti-$CH_2{=}CHNHCH_3$	88	67	70	833	813	809
E-$CH_3CH_2CH{=}CHNH_2$	44	17	17	789	763	755
Z-$CH_3CH_2CH{=}CHNH_2$	43	16	18	792	765	760
$(CH_3)_2C{=}CHNH_2$	32	6	7	755	729	723
E-$CH_3CH{=}C(CH_3)NH_2$	31	5	4	752	726	718
Z-$CH_3CH{=}C(CH_3)NH_2$	24	-2	-4	754	728	721
$CH_2{=}C(CH_2CH_3)NH_2$	31	4	6	784	757	751
E, syn-$CH_3CH{=}CHNHCH_3$	65	38	39	786	760	752
E, anti-$CH_3CH{=}CHNHCH_3$	70	44	44	781	756	747
Z, syn-$CH_3CH{=}CHNHCH_3$	82	56	58	802	776	770
Z, anti-$CH_3CH{=}CHNHCH_3$	69	43	45	785	759	752
anti-$CH_2{=}C(CH_3)NHCH_3$	60	33	33	782	757	750
syn-$CH_2{=}C(CH_3)NHCH_3$	49	22	24	784	758	753
$CH_2{=}CHN(CH_3)_2$	85	58	60	810	783	778
anti-$CH_2{=}CHNHCH_2CH_3$	66	39	42	804	777	771
syn-$CH_2{=}CHNHCH_2CH_3$	61	34	35	809	782	778

[a] Values in kJ mol^{-1}.

[b] The same $\Delta H_{f,298} - \Delta H_{f,0}$ difference for the CBS-Q calculations as for the G2(MP2).

neutral enamine. Conversely, the barrier to interconversion of the *E* and *Z* isomers of the 1-propenylamine radical cation by rotation around the C=C double bond is 77 kJ mol^{-1}, almost 200 kJ mol^{-1} lower than the barrier in the neutral compound.

3.3. Imine radical cations

Introduction of methyl groups at either end of the C=N group lowers the heat of formation by 65–85 kJ mol^{-1} (Table 5), the change decreasing with increasing degree of substitution.

The difference in energy between *cis/trans* isomeric imine radical cations is in most cases only small, which contrasts with the considerable *cis/trans* energy differences observed for neutral imines (Table 5). This may be related to the difference in geometry: the CNH angle in unsubstituted, neutral imines is close to 120°, whereas the radical cations are much closer to linear, with a CNH angle around 155°. We find similar differences between the CNC angles in *N*-substituted imines and imine radical cations.

The preferred conformations of imine radical cations such as propanimine$^{+\cdot}$ are eclipsed; the lower-energy conformer (CCCN dihedral angle of 0°) has the CH_3 group eclipsing the C=N. This resembles the properties of neutral imines [19]. Possible reasons for effects of this nature were discussed by Dorigo et al. [26].

3.4. Imine–enamine energy differences

The calculated heat of formation of each neutral imine is lower than that calculated for the corresponding enamine, but the energy differences (Table 7) are lower than those found for keto–enol pairs. The literature estimates of the vinylamine-acetaldimine energy difference [5–8,20,27] range from 9 to 33 kJ mol^{-1}; our results, 15–17 kJ mol^{-1} (Table 7), are very close to two recent G2 results [7,20].

Table 5
Calculated heats of formation of C_1–C_4 imines and the corresponding radical cations[a]

	Neutral imines[b]			Radical cations		
	G2(MP2)		CBS-Q[c]	G2(MP2)		CBS-Q[c]
	0 K	298 K	298 K	0 K	298 K	298 K
$CH_2{=}NH$	95	87	92	1059	1052	1051
E-$CH_3CH{=}NH$	58	43	47	983	969	967
Z-$CH_3CH{=}NH$	60	46	50	983	970	968
$CH_2{=}NCH_3$	94	79	84	980	967	964
E-$CH_3CH_2CH{=}NH$	45	24	28	958	938	936
Z-$CH_3CH_2CH{=}NH$	49	28	32	957	937	935
$(CH_3)_2C{=}NH$	23	2	5	913	894	890
E-$CH_3CH{=}NCH_3$	57	36	40	914	895	890
Z-$CH_3CH{=}NCH_3$	73	53	57	914	896	891
$CH_2{=}NCH_2CH_3$	74	53	58	944	925	921
E-$CH_3CH_2CH_2CH{=}NH$	32	5	7	939	913	908
Z-$CH_3CH_2CH_2CH{=}NH$	35	8	10	937	911	906
E-$(CH_3)_2CHCH{=}NH$	25	−2	0	927	901	898
Z-$(CH_3)_2CHCH{=}NH$	29	1	3	923	897	893
E-$CH_3CH_2C(CH_3){=}NH$	9	−17	−16	890	865	860
Z-$CH_3CH_2C(CH_3){=}NH$	10	−17	−17	889	864	859
E-$CH_3CH_2CH{=}NCH_3$	44	17	20	892	867	860
Z-$CH_3CH_2CH{=}NCH_3$	61	35	38	891	867	863
$(CH_3)_2C{=}NCH_3$	34	9	11	852	828	822
E-$CH_3CH{=}NCH_2CH_3$	37	10	13	880	855	849
Z-$CH_3CH{=}NCH_2CH_3$	52	26	29	883	858	852
$CH_2{=}NCH_2CH_2CH_3$	60	32	37	921	895	890
$CH_2{=}NCH(CH_3)_2$	46	19	23	907	881	875

[a] Values in kJ mol^{-1}.
[b] Taken from [19].
[c] The same $\Delta H_{f,298} - \Delta H_{f,0}$ difference for the CBS-Q calculations as for the G2(MP2).

The steric preferences are quite different for imines and enamines, and the comparisons in Table 7 are between the more stable geometrical isomers of the appropriate imine and enamine. Quite different results would be obtained if the isomerization involved only migration of the hydrogen atom, as illustrated by the *N*-methylpropenylamine/*N*-methylpropanimine isomers (Fig. 2); the difference between the heats of formation of the *cis–syn* pair is considerably smaller than the difference of the *trans–anti* pair, inasmuch as the lower-energy enamine is *syn*, whereas the lower-energy imine is the *trans* form.

The difference between the heats of formation of imines and enamines increases with substitution on the nitrogen and decreases with increasing degree of substitution on the β-carbon atom of the enamine;

Table 6
Calculated geometries of vinylamine and *trans*-acetaldimine and the corresponding radical cations[a]

	CC	CN	HC(1)	HN	HCN	HNC	HCCN
$CH_2{=}CHNH_2$	1.340	1.400	1.088	1.015, 1.014	113.4	113.2, 113.7	174.1, −4.4
$CH_3CH{=}NH$	1.494	1.283	1.099	1.026	123.2	109.7	120.6, −120.6, 0.0
$CH_2{=}CHNH_2^{+\cdot}$	1.410	1.305	1.087	1.019, 1.018	116.7	122.1, 121.4	180.0, 0.0
$CH_3CH{=}NH^{+\cdot}$	1.490	1.242	1.103	1.022	115.5	149.3	122.0, −122.1, 0.0

[a] Geometry optimization at the MP2(full)/6-31G(d) level.

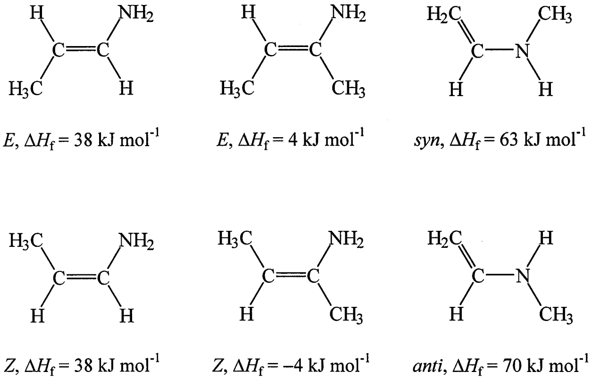

Fig. 1. Geometrical isomerism of propenylamine, butenylamine and *N*-methylvinylamine; energies determined with the CBS-Q method.

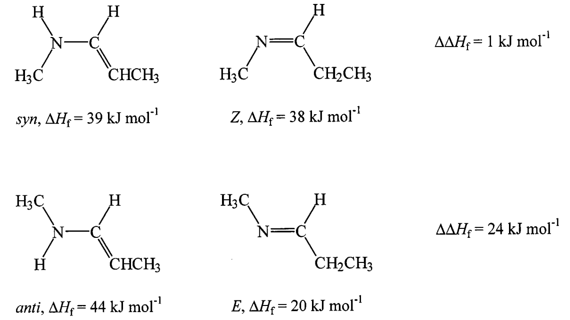

Fig. 2. The influence of stereochemistry on the relative energies of imine–enamine tautomers.

substituents on the α-carbon atom do not change the energy difference significantly.

The relationships are quite different for the radical cations. The heats of formation of the ionized enamines are considerably lower than the heats of formation of the corresponding ionized imines, by between 80 and 170 kJ mol^{-1}. The larger differences are observed when the enamine possesses β substituents, the smaller differences arise when the nitrogen atom carries substituents. The literature estimates of the energy difference between the radical cations of vinylamine and acetaldimine are very close to our result [5,6], as is Bouchoux' estimate for a higher homolog [21]. The enamine-imine radical cation energy differences are considerably larger than the keto-enol radical cation energy differences.

4. Conclusions

The heats of formation of imines and enamines and the corresponding radical cations determined with the G2(MP2) and CBS-Q composite quantum chemical methods show that imines are systematically more stable than enamines, whereas the relationship is reversed for the radical cations. This resembles the relationship observed for keto–enol tautomeric pairs, but the relative energies are considerably different in the two systems (illustrated in Fig. 3), imines being only marginally more stable than enamines, while

Table 7
Energy difference for imine–enamine pairs and the corresponding radical cation pairs[a]

		Neutral molecules		Radical cations	
		G2(MP2)	CBS-Q	G2(MP2)	CBS-Q
$CH_3CH{=}NH$	$CH_2{=}CHNH_2$	17	15	−120	−121
$CH_3CH_2CH{=}NH$	$CH_3CH{=}CHNH_2$	12	10	−151	−155
$(CH_3)_2C{=}NH$	$CH_2{=}C(CH_3)NH_2$	19	19	−112	−112
$CH_3CH{=}NCH_3$	$CH_2{=}CHNHCH_3$	24	23	−82	−81
$CH_3CH_2CH_2CH{=}NH$	$CH_3CH_2CH{=}CHNH_2$	11	10	−148	−151
$(CH_3)_2CHCH{=}NH$	$(CH_3)_2C{=}CHNH_2$	8	7	−168	−170
$CH_3CH_2C(CH_3){=}NH$	$CH_3CH{=}C(CH_3)NH_2$	15	13	−138	−141
$CH_3CH_2C(CH_3){=}NH$	$CH_2{=}C(CH_2CH_3)NH_2$	13	11	−107	−108
$CH_3CH_2CH{=}NCH_3$	$CH_3CH{=}CHNHCH_3$	21	19	−108	−112
$(CH_3)_2C{=}NCH_3$	$CH_2{=}C(CH_3)NHCH_3$	13	13	−71	−72
$CH_3CH{=}NCH_2CH_3$	$CH_2{=}CHNCH_2CH_3$	24	22	−78	−78

[a] $\Delta H_{f,298}$ (enamine) $-$ $\Delta H_{f,298}$ (imine), kJ mol^{-1}. The more stable geometrical isomer of each imine and enamine chosen for comparison.

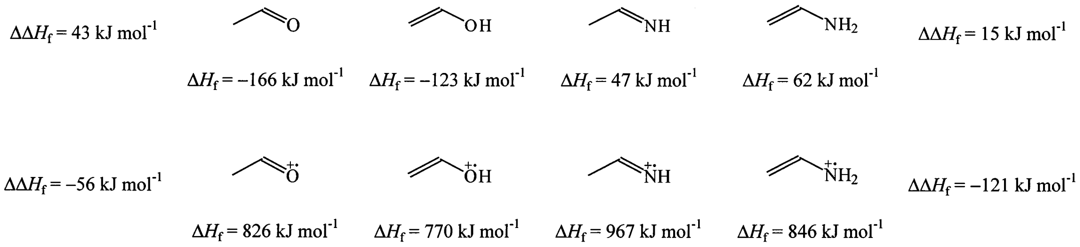

Fig. 3. Simple imine–enamine tautomeric pairs and their oxygen analogs; energies determined with the CBS-Q method.

enamine radical cations are considerably lower in energy than imine radical cations.

Like enol ethers, *N*-substituted enamines show a pronounced preference for a *syn* conformation in which the *N*-alkyl group eclipses the $C{=}C$ double bond; this is not the case for the corresponding radical cations.

References

[1] (a) J.L. Holmes, F.P. Lossing, J. Am. Chem. Soc. 104 (1982) 2648; (b) F. Turecek, in Z. Rappoport (Ed.), The Chemistry of Enols, Wiley, Chichester, 1990, Chap. 3, p. 96.

[2] F. Turecek, C.J. Cramer, J. Am. Chem. Soc. 117 (1995) 12 243.

[3] Y. Apeloig, in Z. Rappoport (Ed.), The Chemistry of Enols. Wiley, Chichester, 1990, Chap. 1, p. 1.

[4] B. Albrecht, M. Allan, E. Haselbach, L. Neuhaus, P.-A. Carrupt, Helv. Chim. Acta 67 (1984) 220.

[5] M.H. Lien, A.C. Hopkinson, Can. J. Chem. 62 (1984) 922.

[6] G. Bouchoux, F. Penaud-Berruyer, M.T. Nguyen, J. Am. Chem. Soc. 115 (1993) 9728.

[7] K. Lammertsmaa, B.V. Prasad, J. Am. Chem. Soc. 116 (1994) 642.

[8] J.-F. Lin, C.-C. Wu, M.-H. Lien, J. Phys. Chem. 99 (1995) 16 903.

[9] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (1988) (suppl. 1).

[10] (a) P.A.S. Smith, The Chemistry of Open-Chain Organic Nitrogen Compounds, Benjamin, New York, 1965, Vol. 1, pp 293–341; (b) Enamines: Synthesis, Structure and Reactions, A.G. Cook (Ed.), Marcel Dekker, New York, 1969.

[11] (a) J.A. Pople, M. Head-Gordon, D.J. Fox, K. Raghavachari, L.A. Curtiss, J. Chem. Phys. 90 (1989) 5622; (b) L.A. Curtiss, K. Raghavachari, G.W. Trucks, J.A. Pople, ibid. 94 (1991) 7221; (c) L.A. Curtiss, P.C. Redfern, B.J. Smith, L. Radom, ibid. 104 (1996) 5148; (d) L.A. Curtiss, K. Raghavachari, P.C. Redfern, J.A. Pople, ibid. 106 (1997) 1063.

[12] L.A. Curtiss, K. Raghavachari, J.A. Pople, J. Chem. Phys. 98 (1993) 1293.

[13] (a)G.A. Petersson, T.G. Tensfeldt, J.A. Montgomery, J. Chem. Phys. 94 (1991) 6091; (b) J.A. Montgomery, J.W. Ochterski, G.A. Petersson, ibid. 101 (1994) 5900; (c) J.W. Ochterski, G.A. Petersson, K. Wiberg, J. Am. Chem. Soc. 117 (1995) 11 299.

[14] J.W. Ochterski, G.A. Petersson, J.A. Montgomery, J. Chem. Phys. 104 (1996) 2598.

[15] S. Hammerum, Int. J. Mass Spectrom. Ion Process. 165 (1997) 63.

[16] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T.A. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. DeFrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez and J.A. Pople, GAUSSIAN 94, revision E2, SGI; Gaussian, Inc., Pittsburgh PA, 1995.

[17] A. Nicolaides, A. Rauk, M.N. Glukhovtsev, L. Radom, J. Phys. Chem. 100 (1996) 17 460.

[18] D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.B. Bailey, K.L. Churney, R.L. Nuttall, J. Phys. Chem. Ref. Data 11 (1982) (suppl. 2).

[19] T. Sølling, S. Hammerum, unpublished.

[20] B.J. Smith, L. Radom, J. Am. Chem. Soc. 114 (1992) 36.

[21] G. Bouchoux, C. Alcaraz, O. Dutuit, M.T. Nguyen, J. Am. Chem. Soc. 120 (1998) 152.

[22] G. Bouchoux, C. Alcaraz, O. Dutuit, M.T. Nguyen, Int. J. Mass Spectrom. Ion Process. 137 (1994) 93.

[23] J.L. Holmes, F.P. Lossing, P.M. Mayer, Chem. Phys. Lett. 198 (1992) 211.

[24] M.T. Nguyen, J. Rademakers, J.M.L. Martin, Chem. Phys. Lett. 221 (1994) 149.

[25] (a) P. Cahill, L.P. Gold, and N.L. Owen, J. Chem. Phys. 48 (1968) 1620; (b) M. Sakakibara, F. Inogaki, I. Harada, T. Shimanouchi, Bull. Chem. Soc. Jpn. 49 (1976) 46; (c) H. Kagan, Organic Stereochemistry, Edward Arnold, London, 1979.

[26] A.E. Dorigo, D.W. Pratt, K.N. Houk, J. Am. Chem. Soc. 109 (1987) 6591.

[27] R.A. Eades, D.A. Weil, M.R. Ellenberger, W.E. Farneth, D.A. Dixon, C.H. Douglas, J. Am. Chem. Soc. 103 (1981) 5372.