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Imine ⇌ Enamine Tautomerism

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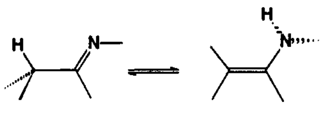
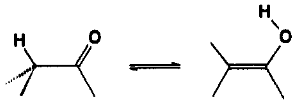
Abstract: Acetaldimine ⇌ vinylamine tautomerism and their conformational preferences are studied using MP2(full)/6-31G* geometries and Gaussian-2 energies. Geometrical parameters, harmonic vibrational frequencies, relative stabilities, conformational stabilities, the amine inversion barrier, ionization energies, atomization energies, and equilibrium constants are compared with experimental gas-phase data when available. Their less than satisfactory agreement results mainly from a lack of definitive experimental data. The imine ⇌ enamine tautomerism is also compared with the keto ⇌ enol and nitro ⇌ *aci*-nitro tautomeric processes. Solvent effects are estimated by Onsager's reaction field model (SCRF) at HF/6-31G* for structural parameters and vibrational frequencies, both of which are minimal, and at QCISD for energies. The *anti*-acetaldimine tautomer is energetically favored over vinylamine by 3.9 kcal/mol at G2 and by 4.3 kcal/mol after extrapolation of the acetonitrile solvent effect. The theoretical (gas-phase) proton affinity of the enamine anion amounts to 377 kcal/mol, and the atomization energy of acetaldimine is 697 kcal/mol. The anti conformation of acetaldimine is energetically preferred over the syn form by <1 kcal/mol, which becomes even less after inclusion of solvent effects. Similarly, the energetic preference of the syn conformer over the anti form of the enamine anion becomes negligible after inclusion of solvent effects. The effect of charges in Coulombic versus resonance delocalization in the allylic enamine anion is discussed in detail.

Tautomerism is one of the fundamental processes in (bio)-organic chemistry that underlies most of the important condensation reactions. The subject of tautomerism has been extensively reviewed[1] but is receiving renewed interest because of improved experimental and theoretical methods, and their recognized importance in biological processes. A barrage of recent theoretical studies has taken place, but the validity of the various levels of theory employed remains a concern. We illustrated this recently in a study on the nitromethane ⇌ *aci*-nitromethane tautomerism[2] for which we used Pople's G1 theory,[3a] which generally gives absolute energies to within 2 kcal/mol of experimental values. For nitromethane the G1 theoretically estimated heats of atomization and of ionization show excellent agreement with experiment. To our surprise similarly reliable data on other tautomeric equilibria was unavailable in the literature except for the acetaldehyde ⇌ vinyl alcohol tautomeric pair. Therefore and because of the important place of tautomeric processes in synthetic chemistry, we now report on the parent acetaldimine ⇌ vinylamine tautomeric process using both G1 and G2 theory[3] and make comparisons with experimental data where possible. Because of the large amount of literature data on tautomeric pairs, we highlight key features of some tautomeric processes in this introduction to illustrate the need for a consistent and comprehensive evaluation.

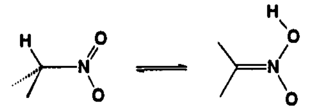
For both keto ⇌ enol and nitro ⇌ *aci*-nitro tautomerisms, the geometries and relative energies depend strongly on the level of theory.[4,5] Even for the parent systems, both large basis sets and extensive electron correlation are required for obtaining geometric and energetic data that compare well with experimental values. For example, the MP2-HF/6-31G* differences in bond distances in *aci*-nitromethane are 0.047 Å for the C–N bond and 0.072 Å for the N–OH bond.[2] Only the correlated nitromethane structure is in good agreement with experimentally determined structures, and the same applies for the vibrational frequencies. The nitromethane – *aci*-nitromethane energy difference (ΔE) varies significantly with the employed level of theory as illustrated by the ΔE values of 14.1 (G1), 19.3 (MP4/6-311++G**//MP2/6-31G*), and 22.9 kcal/mol (MP2/6-31G*). Only the higher G1 level of theory gives atomization and ionization energies in close agreement (<2.5 kcal/mol) with experimental data.[2]



imine/enamine



keto/enol



nitro/*aci*-nitro

Similar observations have been made for the more intensely studied acetaldehyde ⇌ vinyl alcohol tautomerism. Their

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geometries and frequencies are calculated accurately at MP2/6-31G*, but the keto – enol energy difference varies with the theoretical level, albeit to a lesser extent. This is illustrated by the ΔE values of 11.2 (G2), 11.3 (G1), 13.4 (MP4/6-311++G*//HF/6-31+G*), and 16.8 kcal/mol (MP2/6-31G*), all of which differ from the experimentally deduced energy difference of 9.9 ± 2 kcal/mol.[6]

The related imine $\rightleftharpoons$ enamine tautomerism has been the subject of extensive study as well. Generally, the imine dominates the equilibrium, but here also the energy difference between the parent acetaldimine $\rightleftharpoons$ vinylamine tautomers depends strongly on the employed level of theory. For example, Smith and Radom[7] reported recently an energy difference of 4.3 kcal/mol at MP4/6-311+G**//HF/6-31+G* in favor of the imine, which reduces to only 2.0 kcal/mol at CISD/6-31G*,[8] while instead vinylamine is the more stable form at HF/4-31G.[9] Likewise, both the imine conformational stability and amine inversion barrier have not been addressed conclusively[9–12] in spite of a variety of experimental studies.[13–17] For example, in their study Smith and Radom[7] used an HF/6-31+G* optimized geometry of the syn conformer of acetaldimine, whereas earlier Cossé-Barbi et al.[11] had shown that the anti conformation is energetically preferred at post-HF levels. Still earlier, Houk et al.[9] reported that the anti form is the more stable conformer at HF/4-31G, which contrasts with the HF results using several basis sets reported by Cossé-Barbi et al.,[11] while the syn form was calculated[9] to be the most stable conformer of the anion. Of particular concern is the significant difference in the heat of formation of 12.4 kcal/mol for acetaldimine, reported at MP4/6-311+G** by Smith and Radom,[7] and its experimentally deduced value of 2 ± 4 kcal/mol, reported by Farneth, Dixon and co-workers.[18] A theoretical estimate of 375.7 kcal/mol has been reported by Smith and Radom[7] for the ionization of *syn*-acetaldimine to its syn anion; we are not aware of an experimentally determined value.

Computational Methods

Ab initio molecular orbital calculations[19] were carried out using the GAUSSIAN 90 and 92 suite of programs.[20] Acetaldimine (**1**, **2**), vinylamine (**3** (C_1), **4**) and the acetaldimine anion (**5**, **6**) were optimized within C_s symmetry (except for **3** with the split-valence HF/3-21G basis), with the heavy-atom d-polarized HF/6-31G* basis, and with MP2(full)/6-31G*, which includes the effects of all electron correlation using second-order Møller–Plesset perturbation theory. The structures with their geometrical parameters are shown in Figure 1, which also contains the experimentally determined structures that are referred to in the text. We refrain from displaying HF/3-21G geometrical parameters, since these differ substantially in all cases from those obtained at both HF and MP2/6-31G*. Throughout the text we refer to MP2/6-31G* geometries. These are also the basis for the frozen core MP(fc) full fourth-order single-point higher level calculations that employ up to essentially a triply split basis set (6-311G) with d- and hydrogen p-polarization functions (**) and diffuse p- and s-functions (++). At the G1 level[3a] corrections are made to the MP4/6-311G** energy that include additional diffuse functions ($\Delta E(+)$), extra d- and f-functions for non-hydrogen atoms (ΔE(2df)), quadratic configuration interaction (ΔE(QCI or QCISD-(T))), an empirical higher level correlation correction (ΔE(HLC)) based on the number of electrons (HLC = $-0.19n_\alpha - 5.95n_\beta$), and 0.95 scaled[21] zero-point vibrational MP2/6-31G* energy (ZPE) corrections as shown in equation 1—standard G1 and G2 employ the less accurate HF/6-31G* corrected ZPEs. At the G2 level[3b] adjustments to the G1 energy are made that include corrections for the larger 6-311+G(3df,2p) basis set at MP2 and an empirical correction (×1.14 in mhartrees) to HLC for the number of valence electron pairs.

$$\mathrm{G1} = \mathrm{MP4/6\text{-}311G^{**}} + \Delta E(+) + \Delta E(\mathrm{2df}) + \Delta E(\mathrm{QCI}) + \Delta E(\mathrm{HCL}) + \text{scaled ZPE} \quad (1)$$

$$\mathrm{G2} = \mathrm{G1} + \Delta + n\text{-pair correction} \quad (2)$$

$$\Delta = \mathrm{MP2/6\text{-}311{+}G(3df,2p)} - \mathrm{MP2/6\text{-}311G(2df,p)} - \mathrm{MP2/6\text{-}311{+}G(d,p)} + \mathrm{MP2/6\text{-}311G(d,p)}$$

Absolute energies are given in Table 1 and those at G1 and G2 theory in Tables 2 and 3. All relative energies are summarized in Table 4. Ionization energies of the tautomeric **1**–**3** pair to the corresponding anion are given in Table 5. Scaled MP2/6-31G* vibrational harmonic frequencies for the tautomeric structures are given in Table 6, and atomization energies are listed in Table 7.

The bonding properties of all structures were investigated with Bader's topological one-electron density analysis[22,23] using optimized MP2(full)/6-31G* wave functions for **1**–**6**. For each, the one-electron density distribution $\rho(r)$ was analyzed with the aid of the gradient vector field $\nabla\rho(r)$ and the Laplacian $\nabla^2\rho(r)$, which also determines the regions in space wherein electronic charge is concentrated or depleted. Bond critical points are characterized by having a minimum value in $\rho(r)$ along the maximum electron density path connecting two nuclei and are maxima in all other directions. The ellipticity ϵ at such a critical point describes the spatial symmetry of a bond, whereas the total energy density indicates a bond to be covalent ($H(r) < 0$) or ionic ($H(r) > 0$). The properties of the bond critical points of the most relevant structures are listed in Table 8. The electron populations for each element of these structures (charges listed in Table 9 and summarized for some in Figure 2) were

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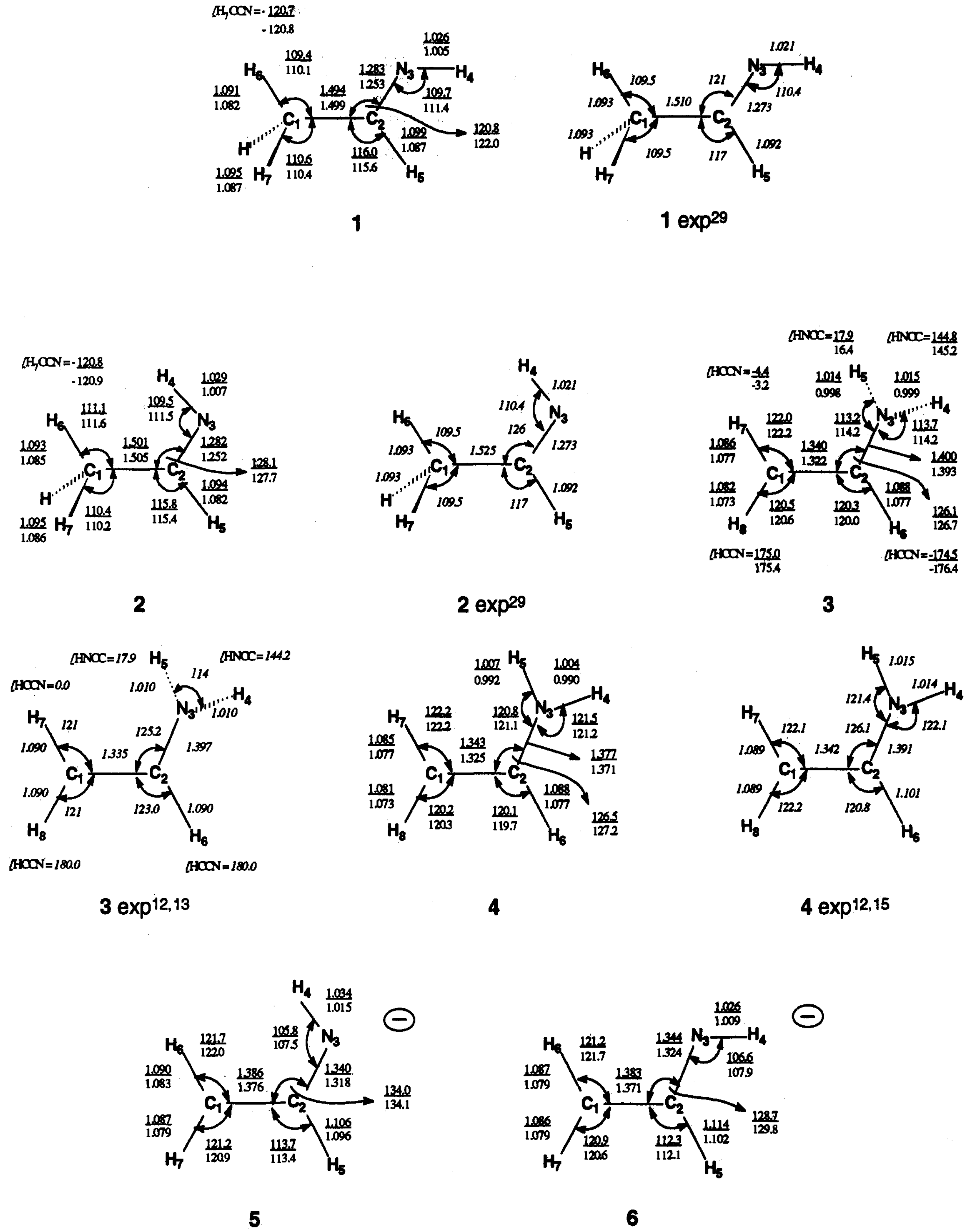

Figure 1. Optimized geometries of **1**–**6**. The top underlined values are the MP2(full)/6-31G* geometrical parameters and the lower values are those at the HF level. Experimental geometrical data are given in italics in separate structures and are taken from the indicated references.

obtained by integration of the charge density within their respective basin as defined by the zero-flux surfaces.

The effect of solvents on the imine $\rightleftharpoons$ enamine tautomerism was studied using Onsager's reaction field model[24] in the framework of the ab initio self-consistent reaction field (SCRF) method as implemented in Gaussian 92.[25] In this model the solute is taken to occupy a spherical cavity of radius a_0 which is calculated quantum mechanically. The solvent is

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Table 1. Absolute Energies (in –hartrees) of the Imine $\rightleftharpoons$ Enamine Tautomers and Their Anion

compd	configuration	HF/3-21G	HF/6-31G*	MP2/6-31G*	MP4/6-31G*[a]	MP4/6-311++G*[a]	ZPE[b]
1	C_s	132.323 00 (0)	133.073 84 (0)	133.503 76 (0)	133.536 56	133.636 70	41.85
2	C_s	132.322 62 (0)	133.072 80 (0)	133.502 72 (0)	133.535 79	133.635 35	41.81
3	C_1		133.061 96 (0)	133.491 28 (0)	133.522 99	133.628 09	41.92
4	C_s	132.326 44 (0)	133.059 20 (1)	133.488 20 (1)	133.519 17	133.624 53	41.12
5	C_s	131.667 51 (0)	132.421 89 (0)	132.859 10 (0)	132.888 59	133.015 25	32.56
6	C_s	131.658 76 (0)	132.415 44 (0)	132.852 67 (0)	132.882 13	133.011 91	32.28

[a] MP2/6-31G* geometries. [b] In kcal/mol and scaled by a 0.95 factor.

Table 2. Total Energies (in –hartrees) and G1 Corrections (in mhartrees) of the Imine $\rightleftharpoons$ Enamine Tautomers and Their Anion

compd	MP4/6-311G**	*E*(+)	*E*(2df)	*E*(QCI)	*E*(HLC)	ZPE[a]	G1
1	133.630 66	–5.72	–68.00	–0.50	–55.26	66.70	133.693 45
3	133.620 69	–7.06	–70.20	–0.95	–55.26	66.80	133.687 37
5	132.989 91	–24.86	–76.01	+0.70	–55.26	51.88	133.093 46
6	132.984 52	–26.94	–76.31	–0.55	–55.26	51.44	133.092 14

[a] MP2/6-31G* ZPEs scaled by a 0.95 factor.

Table 3. Total Energies (in –hartrees) and G2 Corrections (in mhartrees) of the Imine $\rightleftharpoons$ Enamine Tautomers and Their Anion[a]

compd	G1	d,p	+,d,p	2df,p	+3df,2p	Δ	9-p corr	G2
1	133.693 45	133.580 33	133.586 06	133.645 22	133.664 74	13.79	10.26	133.696 98
3	133.687 37	133.571 87	133.579 00	133.638 93	133.659 68	13.62	10.26	133.690 73
5	133.093 46	132.943 66	132.969 10	133.016 20	133.054 45	12.81	10.26	133.096 01
6	133.092 14	132.938 31	132.965 86	133.011 22	133.051 95	13.18	10.26	133.095 06

[a] The G2 corrections to the G1 energies are as follows: (d,p) = MP2/6-311G(d,p); (+,d,p) = MP2/6-+311G(d,p); (2df,p) = MP2/6-311(2df,p); and (+,3df,2p) = MP2/6-311+G(3df,2p). These are summed (see text) in Δ. The 9 val el pair correction is labeled as 9-p corr.

Table 4. Relative Energies (in kcal/mol) of the Imine $\rightleftharpoons$ Enamine Tautomers

compd	HF/3-21G	HF/6-31G*	MP2/6-31G*	MP4/6-31G*	MP4/6-311++G**	MP4/6-311++G** + ZPE corr[a]	G1	G2
1	2.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	2.39	0.65	0.66	0.46	0.48	0.85		
3		7.46	7.83	8.52	5.40	5.47	3.82	3.92
4	0.00	9.18	9.76	10.91	7.64	6.91		

[a] Scaled by a 0.95 factor.

Table 5. Ionization Energies (in kcal/mol) of the Imine $\rightleftharpoons$ Enamine Tautomers

compd	HF/3-21G	HF/6-31G*	MP2/6-31G*	MP4/6-31G*	MP4/6-311++G**	MP4/6-311++G** + ZPE corr[a]	G1	G2
1 → **5**	411.33	409.10	404.53	406.61	389.97	380.68	376.50	377.12
1 → **6**	416.82	413.15	408.56	410.66	392.06	382.49	377.33	377.71
3 → **5**	413.49[b]	401.65	396.70	398.09	384.56	375.20	372.68	373.20
3 → **6**	418.98[c]	405.70	400.73	402.15	386.66	377.02	373.51	373.79

[a] Scaled by a 0.95 factor. [b] Represents **4** → **5**. [c] Represents **4** → **6**.

represented by a continuous dielectric, characterized by a given dielectric constant (ϵ), for which we use the values $\epsilon = 1.0$ (corresponding to the gas phase), $\epsilon = 2.0$ for cyclohexane, $\epsilon = 7.6$ for tetrahydrofuran (THF), and $\epsilon = 35.9$ for acetonitrile. Geometries were optimized at the HF/6-31G level within the SCRF model followed by single-point MP2 and QCISD calculations to include the effects of electron correlation. The influence of the medium on the harmonic vibrational frequencies at HF/6-31G* was investigated, and these frequencies are listed in Table 10. The energies are listed in Table 11 including MP2 single-point energies using MP2/6-31G* (gas-phase) optimized geometries because these differ from the HF/6-31G* geometries. All relative energies are given in Table 12. The solvent effect on the HF/6-31G* atomic charges was analyzed, and these results are listed in Table 13.

Results and Discussion

This sections is arranged to separately discuss the geometrical and electronic features of the tautomeric structures and their common anions, followed by an evaluation of the relative, atomization, and ionization energies of the tautomeric pair and the solvent effect on structures, vibrational frequencies, and energies. MP2/6-31G* geometrical parameters and G2 energies will be used unless noted otherwise.

Acetaldimine (CH_3-CH=NH). Both the *anti*-**1** and *syn*-**2** conformations are equilibrium structures as determined by their all-positive harmonic vibrational MP2/6-31G* frequencies. The anti conformer is energetically favored at *all theoretical levels* with an energy difference of only 0.9 kcal/mol at MP4/6-311++G**//MP2/6-31G*; the discrepancy with the 3-21G and 6-31G* energies reported by Cossé-Barbi et al.[11] is noted.[26] Experimentally, the anti conformer is estimated to be ca. 2 kcal/mol more stable than the syn form.[27,28] The microwave spectrum[29] and both the gas-phase[30] and matrix IR spectra[31] for acetaldimine, also named ethanimine, have been reported. The theoretical geometrical parameters show reasonable agreement with the CC bond lengths and CCN bond angles (*i.e.*, the two derived parameters) obtained from the microwave spectra[29] of both *anti*- and *syn*-acetaldimine (Figure 1). We note that the 1.273 Å assumed CN bond lengths of both experimental structures are shorter than the 1.282(3) Å theoretical values, while the experimental CC bond lengths of both conformers are longer than the theoretical values by 0.016 and 0.024 Å for the anti and syn conformers, respectively. Interestingly, on the basis of HF/

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Table 6. Calculated MP2/6-31G* and Experimental Frequencies (in cm^{-1}) for the Imine $\rightleftharpoons$ Enamine Tautomers[a,b]

anti-acetaldimine (**1**)			vinylamine (**3**)		
calcd	description[c]	exptl[c]	calcd	description[d]	exptl[d]
3292 (2)	NH str a′		3496 (10)	NH_2 str	
3066 (7)	CH_3 str a′	2988	3389 (9)	NH_2 str	
3023 (12)	CH_3 str a″		3161 (10)	CH_2 str	
2951 (54)	CH str a′	2916	3073 (7)	CH str	
2937 (54)	CH_3 str a′	2886	3062 (10)	CH_2 str	2982[e]
1644 (9)	CN str a′	1651	1673 (100)	CC str	1670[f]
1465 (9)	CH_3 def a″		1619 (29)	NH_2 sci	1625[g]
1462 (100)	CH_3 def a′	1454	1422 (2)	CH_2 sci	1454
1402 (17)	CH_3 def a′		1303 (7)	CH bend	
1369 (14)	CH* bend a′	1359	1261 (26)	CCN sci	1254[h]
1246 (37)	CNH bend a′	1250	1052 (9)	NH_2 rock	1080[i]
1090 (4)	CN tor a″	1102	964 (27)	CH wag	1043[j]
1058 (17)	CH_3 rock a″		934 (2)	CH_2 rock	
1039 (27)	CH_3 rock a′	1040	762 (63)	CH_2 wag	809[k]
915 (6)	CC str a′		740 (189)	NH_2 wag	650[l]
665 (61)	CH* OP a″	654	626 (161)	CC tor	575[m]
473 (18)	CCN bend a′		449 (4)	CCN bend	
179 (1)	CC tor a″		332 (57)	CN tor	

[a] The calculated frequencies are uniformly scaled by a 0.95 factor. Intensities are given in parentheses. [b] The main characteristics of the normal modes are given. For more detailed descriptions see the listed references. [c] Reference 30. [d] Reference 14. [e] Observed 2976 and 2987. [f] Observed 1668 and 1672. [g] Uncertain assignment. [h] Observed 1248 and 1260. [i] Observed 1078 and 1084. [j] Observed 1039 and 1046. [k] Observed 805 and 812. [l] Observed 616 and 684. [m] Observed 569 and 580.

Table 7. Atomization Energies (–kcal/mol) of the Imine $\rightleftharpoons$ Enamine Tautomers and Their Anion

structure	G2	G1	experimental
anti-**1**	696.7	694.3	708.7 ± 4
3	692.8	690.5	
anion *syn*-**5**	633.4	631.5	
anion *anti*-**6**	632.8	630.7	

Table 8. Summary of MP2(full)/6-31G* Critical Point Data for the Imine $\rightleftharpoons$ Enamine Tautomers and Their Anion

structure	bond	ϵ	$\rho(r)$	$\nabla^2\rho(r)$	$H(r)$
anti-**1**	C_1–C_2	0.017	1.635	−10.990	−1.236
	C_2–N_3	0.120	2.417	−25.007	−3.790
	N_3–H_4	0.013	2.084	−30.463	−2.572
	C_2–H_5	0.007	1.716	−16.841	−1.560
	C_1–H_6	0.010	1.731	−17.366	−1.560
	C_1–H_7	0.013	1.692	−16.255	−1.498
3	C_1–C_2	0.460	2.278	−23.346	−2.625
	C_2–N_3	0.064	2.007	−22.979	−2.996
	N_3–H_4	0.041	2.192	−38.219	−3.052
	N_3–H_5	0.043	2.196	−38.281	−3.061
	C_2–H_6	0.029	1.876	−24.063	−1.945
	C_1–H_7	0.029	1.826	−22.354	−1.858
	C_1–H_8	0.033	1.847	−23.021	−1.903
anti-**5** anion	C_1–C_2	0.428	2.103	−20.032	−2.219
	C_2–N_3	0.212	2.293	−27.893	−3.541
	N_3–H_4	0.020	2.122	−32.920	−2.810
	C_2–H_5	0.016	1.723	−19.063	−1.639
	C_1–H_6	0.084	1.763	−19.989	−1.753
	C_1–H_7	0.095	1.762	−19.782	−1.759
syn-**6** anion	C_1–C_2	0.415	2.077	−19.328	−2.162
	C_2–N_3	0.197	2.310	−27.963	−3.612
	N_3–H_4	0.015	2.080	−31.935	−2.726
	C_2–H_5	0.021	1.768	−20.454	−1.726
	C_1–H_6	0.097	1.759	−19.721	−1.752
	C_1–H_7	0.090	1.744	−19.416	−1.722

[a] $\rho(r)$ is in e·Å^{-3}; $\nabla^2\rho(r)$ is in e·Å^{-5}; $H(r)$ is in hartree·Å^{-3}.

Table 9. MP2(full)/6-31G* Atomic Properties of the Imine $\rightleftharpoons$ Enamine Tautomers and Their Anion[a]

structure	atom	charge	scaled energy (au)
anti-**1**	C_1	−0.081	−38.026 067
	C_2	0.735	−37.492 894
	N_3	−1.190	−55.147 037
	H_4	0.353	0.473 689
	H_5	0.033	0.600 834
	H_6	0.066	0.583 315
	H_7	0.042	0.590 038
	sum	0.000	133.503 91 (133.503 76)
3	C_1	−0.128	37.994 209
	C_2	0.371	37.737 696
	N_3	−1.186	55.087 765
	H_4	0.393	0.451 367
	H_5	0.394	0.451 552
	H_6	0.054	0.593 876
	H_7	0.042	0.588 793
	H_8	0.057	0.585 795
	sum	−0.003	133.491 05 (133.491 28)
syn-**5** anion	C_1	−0.354	−37.971 136
	C_2	0.531	−37.563 183
	N_3	−1.249	−54.935 046
	H_4	0.235	0.517 192
	H_5	−0.065	0.636 024
	H_6	−0.050	0.616 639
	H_7	−0.049	0.619 656
	sum	−1.001	132.858 88 (132.859 10)
anti-**6** anion	C_1	−0.328	−37.961 486
	C_2	0.509	−37.569 587
	N_3	−1.243	−54.924 341
	H_4	0.237	0.523 168
	H_5	−0.087	0.640 199
	H_6	−0.034	0.612 035
	H_7	−0.053	0.622 163
	sum	−0.999	132.852 98 (132.852 67)

[a] The kinetic energies are corrected for the small virial defect found in the calculations by multiplying them by $-V/T - 1$. The values in parentheses are the total MP2(full)/6-31G* energies.

4-31G calculations, Hashiguchi et al.[30] reversed the conformational assignment, since they obtained the larger calculated CCN angle for the anti form **1**. This is in sharp contrast with our calculations which agree well with the conformational assignments of Lovas et al.[29] (see Figure 1). Whereas the HF and MP2/6-31G* structures are essentially the same, it is noted that the C=N bond is elongated by 0.030 Å in both **1** and **2** when electron correlation is included in the geometry optimization. The analysis of the experimental vibrational spectra is complicated by the fact that both conformers (with possibly additional molecules) are present. Both this uncertainty and the lack of experimental assignments limit a careful analysis. Nevertheless, the gas-phase IR data of Hashigushi et al.[30] (listed in Table 6) differ from those calculated with a root mean square of 'only' 30 cm^{-1}. However, it is evident that a more precise experimental analysis of the acetaldimine conformers **1** and **2** is desired.

The electron density analysis for the C=N bond critical point gives a modest ellipticity ϵ (0.120) and a negative Laplacian $\nabla^2\rho(r)$ as expected for the slightly polarized bond. This is supported by the calculated atomic charges (Table 9, Figure 2),[32] which also show the CH_3 and imine groups to be nearly neutral.

Vinylamine (CH_2=$CHNH_2$). The prototype of enamines, vinylamine, has been the subject of several experimental[13-17] and theoretical[9-12] studies, which concentrated largely on whether the amine group is pyramidalized. The MP2/6-31G* minimum-energy structure **3** has a nonplanar geometry with a significantly pyramidalized amine group (Figure 1) which has an inversion barrier, via planar **4**, of 1.4 kcal/mol at MP4/6-311++G** +

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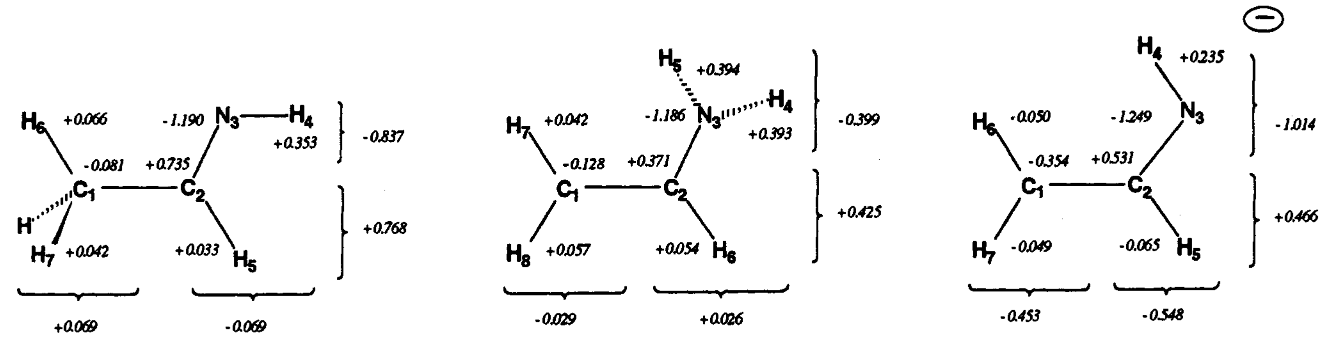
(32) An evaluation of the effect of electron correlation (using MP2 vs HF) and basis set (6-31G*, 6-31G**, and 6-311++G**) has recently been given: Wiberg, K. B.; Hadad, C. M.; Rablen, P. R.; Cioslowski, J. *J. Am. Chem. Soc.* **1992**, *114*, 8644.



1 **3** **5**

Figure 2. Atomic and group charges for the imine ⇌ enamine tautomers and their common anion.

Table 10. Calculated Vibrational HF/6-31G* Frequencies (ν in cm^{-1}) and Infrared Intensities (i in km/mol, in Parentheses) for **1**–**6**[a]

1		**2**		**3**		**4**		**5**		**6**	
$\epsilon = 1.0$	$\epsilon = 35.9$	$\epsilon = 1.0$	$\epsilon = 35.9$	$\epsilon = 1.0$	$\epsilon = 35.9$	$\epsilon = 1.0$	$\epsilon = 35.9$	$\epsilon = 1.0$	$\epsilon = 35.9$	$\epsilon = 1.0$	$\epsilon = 35.9$
$\nu(i)$	$\Delta\nu(\Delta i)^b$	$\nu(i)$	$\Delta\nu(\Delta i)^b$	$\nu(i)$	$\Delta\nu(\Delta i)^b$	$\nu(i)$	$\Delta\nu(\Delta i)^b$	$\nu(i)$	$\Delta\nu(\Delta i)^b$	$\nu(i)$	$\Delta\nu(\Delta i)^b$
A′		A′		A		A′		A′		A′	
3350 (1)	−5 (0)	3321 (2)	−5 (1)	3488 (11)	0 (9)	3598 (46)	−6 (25)	3185 (122)	−8 (30)	3235 (113)	1 (28)
2983 (20)	−6 (13)	2967 (70)	−2 (15)	3399 (11)	0 (8)	3485 (51)	−5 (33)	2978 (142)	8 (30)	2991 (136)	−3 (24)
2907 (63)	13 (−8)	2948 (3)	2 (3)	3079 (24)	−4 (10)	3080 (25)	−5 (15)	2922 (37)	5 (6)	2938 (36)	−3 (16)
2886 (20)	3 (1)	2881 (15)	4 (−2)	3023 (13)	0 (2)	3023 (13)	1 (1)	2798 (209)	−2 (55)	2711 (249)	26 (10)
1730 (89)	−8 (37)	1731 (94)	−9 (41)	2998 (12)	−2 (4)	2999 (13)	−3 (2)	1560 (578)	−12 (132)	1599 (440)	−11 (106)
1456 (9)	0 (3)	1462 (22)	−3 (15)	1699 (149)	−7 (68)	1687 (267)	−12 (132)	1438 (36)	−1 (20)	1432 (30)	0 (8)
1427 (34)	1 (15)	1409 (17)	2 (8)	1642 (32)	1 (6)	1626 (27)	2 (7)	1352 (42)	−4 (18)	1328 (222)	−2 (15)
1386 (9)	1 (4)	1387 (6)	3 (0)	1433 (2)	1 (1)	1433 (3)	0 (4)	1263 (219)	−6 (116)	1279 (223)	−9 (230)
1249 (33)	7 (5)	1259 (70)	6 (21)	1310 (4)	0 (2)	1307 (13)	−1 (11)	1131 (26)	1 (25)	1119 (40)	0 (24)
1042 (28)	3 (6)	1041 (25)	3 (5)	1262 (42)	0 (17)	1242 (84)	2 (42)	962 (3)	0 (4)	973 (31)	−1 (19)
890 (6)	1 (2)	880 (1)	1 (0)	1050 (10)	0 (2)	1024 (39)	3 (11)	487 (19)	0 (3)	486 (6)	−1 (3)
471 (20)	−2 (7)	477 (10)	0 (3)	1011 (21)	3 (1)	935 (6)	3 (2)	A″		A″	
A″		A″		940 (6)	1 (2)	441 (2)	2 (1)	1065 (5)	−3 (−1)	1036 (3)	4 (0)
2927 (31)	4 (−3)	2934 (24)	6 (−5)	866 (95)	−15 (54)	A″		757 (96)	−10 (0)	698 (1)	0 (0)
1460 (8)	0 (−1)	1455 (7)	−2 (3)	745 (148)	−9 (24)	1020 (11)	4 (0)	598 (1)	4 (1)	541 (148)	−5 (−7)
1130 (9)	2 (0)	1137 (46)	−1 (2)	623 (216)	−11 (101)	827 (96)	−26 (3)	378 (149)	34 (17)	369 (58)	8 (33)
1065 (22)	−3 (2)	1071 (20)	−2 (6)	452 (5)	−1 (2)	686 (8)	−1 (3)				
671 (56)	−1 (14)	684 (19)	0 (5)	310 (64)	−1 (24)	364 (13)	15 (−2)				
175 (3)	3 (1)	160 (0)	−1 (0)			488i (335)	16 (42)				

[a] The frequencies are scaled by a 0.90 factor and are listed in descending order, grouped by A′ and A″ symmetries. [b] Frequency shifts ($\Delta\nu$) from the gas phase ($\epsilon = 1$) to acetonitrile ($\epsilon = 35.9$) are listed with the associated changes in intensities in parentheses (Δi).

scaled ZPE. The geometrical parameters of **3** compare remarkably well with those obtained from a microwave spectrum,[13] considering that the vinyl group was assumed as planar symmetric and that only the CN bond length and CCN bond angle were treated as variables in the experimental structure. Similarly, the theoretical structure of planar **4** and that obtained from microwave measurements[12,13] agree very well with the possible overestimation of the experimental CN bond length of 1.391 Å. The calculated 1.4 kcal/mol inversion barrier is in close agreement with the 'best' estimates of 1.1 kcal/mol (390 cm^{-1}) by Brown et al.[15] and 1.1 kcal/mol (375 cm^{-1}) by Meyer.[12] Both were based on theoretical treatments of the microwave spectrum reported by Lovas et al.[13] These inversion barriers are likely to be an underestimate because the experimental equilibrium geometry **3** was assumed to have a planar symmetrical vinyl group, contrasting our theoretical finding. A slightly larger 2.1 kcal/mol (740 cm^{-1}) barrier was determined from an infrared study by Hamada et al.[14] Here again it is relevant to stress that a good structural agreement only results when electron correlation is included in the geometry optimization using a polarized basis set. This is immediately evident from a comparison with HF/6-31G* data (*e.g.*, $\Delta_{\text{MP2-HF}}(\text{C=C}) = 0.018$ Å, Figure 1) and those reported with a variety of different basis sets.[7,9-12,18b] However, a 'pyramidal' structure **3** is obtained with all basis sets but 3-21G. An exception is the study by Sevin et al.,[10a] who found only planar structures with four different basis sets. Planar structure **4** was characterized as a transition structure with one imaginary HF and MP2/6-31G* frequency for nitrogen pyramidalization. As before, the molecular structure can also be assessed by comparing theoretical and experimental vibrational frequencies. In the case of vinylamine **3**, such an evaluation was performed by Hamada et al.[14] but they found a large discrepancy between the limited set of observed frequencies and those calculated with the 4-31G basis set. Similar to the case of acetaldimine, this may be contributed to both the likely presence of contaminants in the experiment and an inadequate theoretical treatment. The MP2/6-31G* frequencies (Table 6) do show a much better agreement with those observed experimentally (*i.e.*, root mean square 52 cm^{-1} for 10 frequencies), but they also underscore the need for improved detection of the infrared spectrum of **3**.

The electron density analysis gives a ϵ value of 0.460 and thereby underscores the C=C double-bond character. The significant electronegativity of the nitrogen is evident from the +–+ charge distribution (Table 9) in the H_2NC unit, while the CH_2 and $HCNH_2$ units are both essentially neutral (Figure 2).

Acetaldimine Anion. Both the syn (**5**) and anti conformations (**6**) of this anion are equilibrium structures. The syn conformer is energetically favored at all levels of theory with an energy difference of 0.6 (0.8) kcal/mol at G2 (G1). A similar energy difference of 0.9 kcal/mol (G1) has been calculated for the syn and anti conformations of the isoelectronic neutral vinyl alcohol.[33] The geometrical parameters of **5** and **6**, and in particular the 'allylic' CCN bond lengths, are, like the cases of all other structures in this study, influenced by the effects of electron correlation

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(33) Lammertsma, K.; Prasad, B. V. Unpublished results.

Table 11. Calculated 6-31G* Energies (in –hartrees), Dipole Moments (μ in D), and Cavity Radii (a_0 in Å) of Imine $\rightleftharpoons$ Enamine Tautomers and Their Anion

compd	a_0	ϵ	μ^a	HF	MP^b	MP^c	QCISD^b
1	3.36	1.0	1.9	133.073 84	133.489 14	133.501 97	133.522 42
		2.0	2.0	133.074 47	133.489 67	133.502 46	133.522 95
		7.6	2.1	133.075 19	133.490 30	133.503 03	133.523 58
		35.9	2.2	133.075 46	133.490 53	133.503 24	133.523 82
2	3.36	1.0	2.4	133.072 80	133.488 14	133.500 97	133.521 55
		2.0	2.5	133.073 68	133.488 93	133.501 70	133.522 33
		7.6	2.6	133.074 71	133.489 87	133.502 55	133.523 26
		35.9	2.7	133.075 09	133.490 22	133.502 86	133.523 61
3	3.34	1.0	1.5	133.061 96	133.477 24	133.490 21	133.510 08
		2.0	1.6	133.062 27	133.477 55	133.490 51	133.510 38
		7.6	1.6	133.062 62	133.477 90	133.490 85	133.510 71
		35.9	1.7	133.062 76	133.478 03	133.490 97	133.510 82
4	3.36	1.0	1.7	133.059 20	133.474 16	133.487 22	133.506 48
		2.0	1.8	133.059 58	133.474 55	133.487 58	133.506 84
		7.6	1.9	133.060 05	133.475 02	133.488 03	133.507 27
		35.9	2.0	133.060 23	133.475 20	133.488 19	133.507 43
5	3.48	1.0	1.4	132.421 89	132.845 22	133.856 61	132.872 64
		2.0	1.5	132.422 16	132.845 48	133.856 88	132.872 91
		7.6	1.6	132.422 48	132.845 79	133.857 20	132.873 23
		35.9	1.7	132.422 61	132.845 92	133.857 33	132.873 36
6	3.44	1.0	2.0	132.415 44	132.838 85	133.852 67	132.866 41
		2.0	2.1	132.416 09	132.839 34	133.853 14	132.866 93
		7.6	2.2	132.416 82	132.839 88	133.853 68	132.867 51
		35.9	2.3	132.417 08	132.840 08	133.853 87	132.867 72

[a] MP2/6-31G*//HF/6-31G* dipole moments. [b] Using 'solvent' HF/6-31G* optimized geometries. [c] Using 'gas-phase' MP2/6-31G* optimized geometries.

Table 12. Solvent Effect on the 6-31G* Energy Differences (in kcal/mol) between Imine $\rightleftharpoons$ Enamine Tautomers, Their Conformers, NH_2-Inversion Barriers, Their Anion Conformers, and Ionization Energies[a]

method	ϵ	tautomers ΔE(**1**–**3**)	conformers ΔE(**1**–**2**)	NH_2-inversion ΔE(**3**–**4**)	anion conformers ΔE(**5**–**6**)	ionization ΔE(**1**–**5**)
HF	1.0	7.46	0.65	1.73	4.04	409.11
	35.9	7.97	0.23	1.59	3.47	409.67
MP2	1.0	7.47	0.62	1.93	3.99	404.07
	35.9	7.84	0.20	1.78	3.66	404.50
MP2^b	1.0	7.38	0.63	1.88	2.47	404.97
	35.9	7.70	0.24	1.74	2.17	405.32
QCISD	1.0	7.74	0.55	2.26	3.91	407.74
	35.9	8.16	0.13	2.13	3.53	408.17

[a] Using solvent-optimized HF/6-31G* geometries. [b] Using 'gas-phase' MP2/6-31G* optimized geometries.

(Figure 1). The CC and CN bond lengths indicate significant double-bond character, thereby suggesting a classic allylic conjugative stabilization of the negative charge, which is supported by simple MO arguments and by the significant ϵ and ρ values of their bond critical points. However, a new reasoning was introduced in a recent study by Wiberg et al.[4b] who convincingly argued that allylic-type anions, which have a much lower resonance energy than allylic-type cations, instead benefit more from internal Coulombic (–+–) stabilization. In a still more recent study of the substituent effect at (neutral) carbonyl groups using correlated (MP2) wave functions, Wiberg et al.[32] concluded that the oxygen is mainly a spectator as far as the properties of the carbonyl group are concerned and that its principal role is to polarize the CO bond leading to an electron deficient carbon. They also demonstrated that the carbonyl group is composed of approximately equal σ and π components. The importance of electron correlation on charge density distributions has recently been underscored.[34] In the present study we also employ correlated wave functions. The MP2/6-31G* atomic charges of syn anion **5** are listed in Table 9 and displayed in Figure 2. Several observations are made. Firstly, the negative charge is similarly distributed over the CH_2 (0.453e) and CHNH (0.548) groups with an expected slight shift to the group containing the more electronegative element. Secondly, the accumulation of charge is 0.424e (0.386e) for the CH_2 group of anion **5** (**6**) as compared to the same methylene group in neutral vinylamine **3**. For the CHNH group this same difference in charge amounts to 0.479e (0.515e) on comparing anion *syn*-**5** (*anti*-**6**) with neutral *anti*-**1**. Thirdly, the –+– charge separation for the CCN frame in *syn*-**5** (Δ(CC) = 0.885e, Δ(CN) = 1.780e) and *anti*-**6** (Δ(CC) = 0.837e, Δ(CN) = 1.752e) is similar to that in neutral *syn*-**1** (Δ(CC) = 0.816e, Δ(CN) = 1.925e). Lastly, the difference in hydrogen charges between anion **5** and vinylamine **3** is 0.476e, which together with the 0.393e charge of the amine proton of **5** accounts for 0.869e of the full unit charge that results in the ionization to anion **5**. These arguments then seem to suggest that there is no special charge (–+–) effect in anion **5** (nor in **6**) and that this in essence may reflect the CN charge (+–) effect extended by conjugation and thereby appears to corroborate Wiberg's recent study on ketones.

Acetaldimine $\rightleftharpoons$ Vinylamine Tautomerism. The estimated energy difference between tautomers **1** and **3** amounts to only 3.9 (3.8) kcal/mol at G2 (G1) in favor of the imine. We are unaware of an experimentally determined value for this parent system. The G2 energy difference is 1.6 kcal/mol smaller than the 5.5 kcal/mol calculated at MP4/6-311++G**//MP2/6-31G* (+ZPE correction). The G2 (G1) theoretical estimate for the atomization energy of imine **1** is –696.7 (–694.3) kcal/mol, which differs significantly (by 12 (14.4) kcal/mol) from the experimental value of –708.7 kcal/mol (Table 7).[35] This suggests the need for a reevaluation of the experimentally deduced heat of formation of acetaldimine **1** of ΔH(298) = 2 ± 4 kcal/mol.[37] This is further underscored by our recent study[2] on nitromethane for which a good agreement was obtained between the G1 calculated heat of atomization of –570.7 kcal/mol and the experimental value of –573.1 kcal/mol.

The G2 (G1) estimated gas-phase ionization (deprotonation) energy is 377.1 (376.5) kcal/mol for *anti*-acetaldimine and 373.2 (372.7) kcal/mol for vinylamine.[39] No experimental values are available, but the theoretical estimates are in line with expectations. For example, the experimental gas-phase ionization energy is 390 ± 3 kcal/mol for propene and 366 ± 3 kcal/mol for acetaldehyde.[40]

From the relative energies and entropies of the tautomers, an estimated gas-phase tautomeric equilibrium constant for acetaldimine is obtained of K_{enamine} = 2.66. We are unaware of an experimental estimate.

Solvent Effects. Tautomeric equilibria, energy differences in rotamers, vibrational frequencies, and even structural parameters are medium-dependent, as has been shown by ab initio SCRF

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(34) Wiberg, K. B.; Hadad, C. M.; LePage, T. J.; Breneman, C. M.; Frisch, M. J. *J. Phys. Chem.* **1992**, *96*, 671.

(35) For the experimental values were used ΔH_f(acetaldimine) = +2 kcal/mol and the heats of formation (0 K) given in the JANAF tables.[36] The theoretical atomization energies ($\sum D_0$) were calculated from the G2 and G1 absolute energies of the molecules and their elements.

(36) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data for Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.

(37) This value is based on ΔH_f(298) = 156 ± 4 kcal/mol for protonated acetaldimine, measured from appearance potentials,[38] and a proton affinity of 213.2 ± 2 kcal/mol, measured by ion cyclotron resonance and relative to a proton affinity for ammonia of 203.6 kcal/mol.[18a]

(38) Bowen, R. D.; Williams, D. H.; Hvistendahl, G. *J. Am. Chem. Soc.* **1977**, *99*, 7509. Solka, B. H.; Russell, M. E. *J. Phys. Chem.* **1974**, *78*, 1268.

(39) Smith and Radom[7] report a gas-phase ionization energy at MP4/6-311+G**//HF/6-31G* (+ZPE correction) for acetaldimine of 379.8 kcal/mol and for *syn*-vinylamine of 375.7 kcal/mol. The corresponding ionization energies at MP4/6-311++G**//MP2/6-31G* (+ZPE correction), using a 'correlated' geometry instead and extra diffuse functions for hydrogens, are 382.5 for **1** and 375.6 kcal/mol for **4**, respectively (see Tables 2 and 4).

(40) (a) Lias, S. G.; Bartmess, J. E.; Liebmann, J. F.; Holmes, J. F.; Levin, R. D.; Mallard, W. G. Gas-phase Ion and Neutral Thermochemistry. *J. Phys. Chem. Ref. Data* **1988**, Suppl. 1. (b) Oakes, J. M.; Jones, M. E.; Bierbaum, V. M.; Ellison, G. B. *J. Phys. Chem.* **1983**, *87*, 4810.

Table 13. Calculated HF/6-31G* Atomic Charges of Imine ⇌ Enamine Tautomers and Their Anion[a]

	1		**2**		**3**		**4**		**5**		**6**	
atom	$\epsilon = 1$ charge	$\epsilon = 35.9$ Δ	$\epsilon = 1$ charge	$\epsilon = 35.9$ Δ	$\epsilon = 1$ charge	$\epsilon = 35.9$ Δ	$\epsilon = 1$ charge	$\epsilon = 35.9$ Δ	$\epsilon = 1$ charge	$\epsilon = 35.9$ Δ	$\epsilon = 1$ charge	$\epsilon = 35.9$ Δ
C_1	0.063	0.001	0.044	0.004	0.037	0.000	0.070	−0.019	−0.245	0.013	−0.212	−0.003
C_2	0.981	−0.003	0.988	−0.009	0.441	0.009	0.460	0.027	0.794	−0.021	0.765	−0.002
N_3	−1.423	0.003	−1.413	−0.016	−1.318	−0.004	−1.423	−0.005	−1.478	−0.001	−1.466	−0.008
H_4	0.364	−0.001	0.354	−0.001	0.398	0.000	0.434	0.004	0.231	−0.003	0.227	0.003
H_5	−0.006	−0.001	0.016	−0.005	0.399	0.001	0.435	0.010	−0.103	−0.003	−0.128	0.014
H_6	0.027	0.000	−0.005	0.006	0.026	−0.007	0.019	0.001	−0.099	0.005	−0.080	−0.012
H_7	−0.002	0.000	0.008	0.011	0.000	0.000	−0.005	−0.004	−0.100	0.008	−0.106	0.009
H_8	−0.002	0.000	0.008	0.011	0.016	0.000	0.011	−0.014				
total	0.002	−0.001	0.000	0.001	−0.001	−0.001	0.001	0.000	−1.000	−0.002	−1.000	0.001

[a] The Δ values are the changes in atomic charge in going from the $\epsilon = 1$ to the $\epsilon = 35.9$ column.

molecular orbital calculations for, *e.g.*, formamide,[41] sulfamic acid,[42] methyl formate,[43] methyl acetate,[43] and substituted vinylamines.[44] It is therefore important to also evaluate the solvent effect on the acetaldimine ⇌ vinylamine tautomerism. All geometry optimizations were carried out at HF/6-31G* in four different dielectric media with $\epsilon = 1.0, 2.0, 7.6$, and 35.9, but the resulting differences in geometrical parameters are extremely small; similar observations have been made by Wiberg and coworkers for formamide and formamidic acid.[41] The influence of the dielectric medium is also modest for most of the HF/6-31G* vibrational frequencies. Table 10 lists these generally small differences (Δ) in calculated frequency (in cm^{-1}) and intensity (in parentheses, in km/mol) between the gas phase and acetonitrile ($\epsilon = 35.9$). The most pronounced are the small red shifts in the polar medium for the CN stretch of **1** ($\Delta = 8$ (37) cm^{-1}) and **2** ($\Delta = 9$ (41) cm^{-1}), the CC stretch of **3** ($\Delta = 7$ (68) cm^{-1}) and **4** ($\Delta = 12$ (132) cm^{-1}), and the CH_2 rock of **3** ($\Delta = 15$ (54) cm^{-1}) and **4** ($\Delta = 26$ (3) cm^{-1}), whereas blue shifts are calculated for the CH_2 rock of **5** ($\Delta = 34$ (17) cm^{-1}) and the HCN bend of **6** ($\Delta = 26$ (10) cm^{-1}). The intensities increase in all bands as a function of the dielectric medium.

The effects of electron correlation were included in the energy evaluations of **1**–**6** at MP2 and QCISD using the HF/6-31G* solvent-optimized geometries. Because the 'correlated' structures differ from those obtained at HF, the MP2 calculations were also carried out with MP2/6-31G* 'gas phase' ($\epsilon = 1$) structures, but the effect of these structural differences on relative energies appears to be minimal. Several observations are made. Firstly, the conformational stabilities are influenced by the solvent. The QCISD (HF) energy difference between the *anti*-**1** and *syn*-**2** conformations reduces from 0.55 (0.65) kcal/mol in the gas to only 0.13 (0.23) kcal/mol at $\epsilon = 35.9$ (acetonitrile) and when extrapolated to MP4/6-311++G** becomes virtually insignificant. A similar reduction of 0.38 (0.57) kcal/mol is calculated for the energy difference between the *syn*-**5** and *anti*-**6** conformations of the anion, but it remains a sizable 3.53 (3.47) kcal/mol. However, *syn*-**5** is only 0.59 kcal/mol more stable than the anti form at G2, and therefore extrapolation of the acetonitrile solvent effect renders a conformational energy difference of a mere 0.2 kcal/mol. Related, but larger reductions in energy differences (≤5 kcal/mol) have been calculated for the *E*/*Z* conformers/isomers of methyl formate,[43] methyl acetate,[43] and disubstituted ethylenes[44] upon solvation in acetonitrile. Secondly, the QCISD (HF) energy difference between the tautomeric pair **1** and **3** of 7.74 (7.46) kcal/mol in the gas phase increases by 0.42 (0.53) kcal/mol in going to acetonitrile, which when added to the G1 value, gives a 4.3 kcal/mol energetic preference of acetaldimine over vinylamine. Somewhat larger increases in tautomeric energy differences have been calculated for solvation of the related formamide and sulfamic acid tautomers. Thirdly, the solvent effect ($\epsilon = 1.0 \rightarrow 35.9$) is negligible for the conformational stability of vinylamine (*i.e.*, $\Delta E_{(3-4)} = 0.13$ kcal/mol), and lastly, it is similarly small ($\Delta E_{(1-5)} = 0.13$ kcal/mol) for the deprotonation of acetaldimine **1**.

Table 14. Summary of G2 (G1) Energies (kcal/mol) for the Prototypic Tautomerisms

tautomeric pairs	ΔE [a]	P.A.[b]	ΣD_0[c]
imine ⇌ enamine	3.9 (3.8)	377.1 (376.5)	−696.7 (−694.3)
keto ⇌ enol	10.8 (10.9)	365.9 (365.0)	−643.4 (−641.4)
nitro ⇌ *aci*-nitro	14.1 (14.1)	355.9 (355.2)	−572.7 (−570.7)

[a] Tautomeric energy differences. [b] Lowest anion proton affinities. [c] Atomization energies of the most stable tautomers.

The solvent effect is also evident in the electron density analyses of **1**–**6**. Particularly, the HF/6-31G* atom charges reveal an increased polarization in acetonitrile of *syn*-**2** as compared to *anti*-**1**, which concurs with a reduced energy difference in a more polar environment. Whereas both anion conformers polarize with larger dielectric constants, the effect is mainly in the CC bond of *syn*-**5**, while the polarization in *anti*-**6** occurs largely on the CC hydrogens. Consequently, **6** benefits more from polar solvation. It is also noted that with progressively more polar solvents the increase in dipole moment μ is larger for both *anti*-**1** and *syn*-**5** than for their corresponding conformers. The opposite is found for the tautomers **1** and **3**, and this explains their increased energy difference in polar media.

Conclusions. It is demonstrated that for the prototypic tautomeric pair, acetaldimine ⇌ vinylamine, meaningful comparisons between theory and experiment result only when (a) geometry optimizations include electron correlation and (b) both large basis sets and extensive electron correlation are used to obtain reliable energy estimates.

The 'correlated' geometrical parameters and harmonic vibrational frequencies of acetaldimine and vinylamine compare well with microwave and matrix/gas-phase IR spectroscopic data. The less than satisfactory agreement for the CC and CN bonds may, in part, be due to assumptions made in the analyses of the microwave spectra, but the 1.1 kcal/mol NH_2 inversion barrier of vinylamine that has been deduced from microwave spectra compares well with the theoretical estimate. The differences between calculated and observed vibrational frequencies for both the conformers of acetaldimine and vinylamine suggest the need for more precise experimental analyses. For the tautomeric pair the calculated solvent effect is small on both the structural parameters and the vibrational frequencies where the red shifts in the CN and CC stretches are the most pronounced.

The energy difference between the acetaldimine and vinylamine tautomers was calculated with G2 theory and is listed in Table 14 together with those of the earlier studied acetaldehyde ⇌

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(41) Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 1645.

(42) Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 523.

(43) Wiberg, K. B.; Wong, M. W. *J. Am. Chem. Soc.* **1993**, *115*, 1078.

(44) Pappalardo, R. R.; Sánchez Marcos, E.; Ruiz-López, M. F.; Rinaldi, D.; Rivail, J.-L. *J. Am. Chem. Soc.* **1993**, *115*, 3722. Pappalardo, R. R.; Sánchez Marcos, E. *J. Chem. Soc., Faraday Trans. 1* **1991**, *87*, 1719.

vinyl alcohol and nitromethane ⇌ *aci*-nitromethane pairs.[45] This table further summarizes for each set the anion proton affinity of the most stable tautomer of which also the atomization energies are listed. The G2 theoretical estimates show excellent agreements with experimental data for both the keto ⇌ enol and nitro ⇌ *aci*-nitro pairs, but the agreement is less than satisfactory for the imine ⇌ enamine pair. It is suggested that the discrepancy lies in experimental uncertainties and calibration. The solvent effect, as estimated by SCRF at QCISD/6-31G* for acetonitrile, increases the G2 energy difference between acetaldimine and vinylamine by ca. 0.4 kcal/mol to an extrapolated 4.3 kcal/mol.

The *anti*-acetaldimine conformer **1** is more stable than its syn conformer **2** by 0.9 kcal/mol at MP4/6-311++G** (+ZPE), which is in excellent agreement with experiment. This energy difference reduces to only 0.5 kcal/mol after extrapolation of the acetonitrile solvent effect. In contrast, the syn conformer of the anion (**5**) is more stable than the anti form (**6**), but the energy difference becomes negligible after inclusion of the solvent (ϵ = 35.9) effect. Analysis of the atom and group charges in these enamine anions suggests that there is no special charge (−+−) effect other than an extension by conjugation (or resonance) of the already present charge (+−) (or polarization) effect in the imine bonds of acetaldimine.

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[45] The G2 energies (with MP2/6-31G* ZPE corrections) are for acetaldehyde $E = -153.57621$ au, for vinyl alcohol $E = -153.55900$ au, for nitromethane $E = -244.67905$ au, and for *aci*-nitromethane $E = -244.65651$.