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Investigation of the Structure and the Properties of Ammeline, Melamine, and 2,4-Diamino-1,3,5-triazine by ab Initio Calculations

Yin Wang, C. U. Pittman, Jr.,* and Svein Saebo

Department of Chemistry, Mississippi State University, Mississippi State, Mississippi 39762

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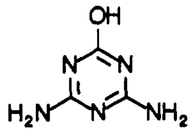
Ammeline, melamine, and 2,4-diamino-1,3,5-triazine have been studied by ab initio calculations at the SCF-level using several different basis sets. It is predicted that melamine has pyramidal amino groups (one up, and two down) with angles between the C–N bond and the NH_2-plane of 12.2° (one) and 9.9° (two) using the 6-31G** basis set. It is also predicted that the amino groups of ammeline and 2,4-diamino-1,3,5-triazine were planar. The hydroxy tautomer of ammeline, **1**, is predicted to be 4.82 kcal/mol more stable than the carbonyl tautomer, **2**, and 23.8 kcal/mol more stable than the quinoid carbonyl tautomer, **11**. The experimental literature is discussed in this context. Both protonated ammeline and deprotonated ammeline were also studied. The calculations predicted that the protonation of ammeline occurred on the ring nitrogens. Even triprotonated ammeline is protonated only at the ring nitrogens. The hydroxyl group of ammeline was more acidic than that of phenol. The energy change of the isodesmic proton transfer from ammeline to phenoxide was −10.11 kcal/mol (6-31G** basis set). The amino groups are significantly pyramidal in the optimized geometry of the ammeline anion. The angle between the C–N bond and the NH_2 plane was 43.9°. This causes the amino groups of the anion to be far more nucleophilic toward formaldehyde than those of ammeline itself.

Introduction

Ammeline, **1**, was first prepared by Liebig in the early 1830s.[1] Ammeline can be prepared in the laboratory by hydrolysis of melamine in aqueous acidic or basic solutions.[2] Ammeline is not soluble in most organic solvents, and is only slightly soluble in hot DMSO or hot water. However, solutions of high concentration can be obtained in mineral acid solutions or hot caustic solutions.[2] The high solubility in acidic solutions is related to the basicity of its triazine ring nitrogens. The solubility in aqueous caustic solutions is believed to be due to the removal of the acidic proton of the hydroxy group.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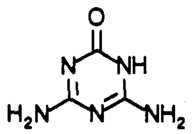
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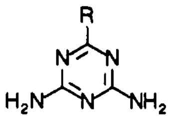
Coexisting with hydroxy structure **1**, is tautomer **2**, 4,6-diamino-1,3,5-triazin-2(1*H*)-one, which is the name now used by Chemical Abstract Services. The earlier studies of the structure of ammeline were conducted by both UV and IR spectroscopy.[3] Shifting of certain absorptions was observed at different pH values. However, no detailed structural information is available which unequivocally establishes the following: (1) which tautomer, **1** or **2**, is the most stable structure of ammeline; (2) how the basicity of the ring nitrogens compares to the amino group nitrogens; and (3) what the specific structural effects of protonation or deprotonation of ammeline are and, in turn, how these processes effect its chemical properties.

Monocharzh[4] calculated the ionization potential of ammeline to be 9.8 eV by the P–P–P technique, a semiempirical method.[5] Novák and Dobás have experimentally measured the pK_bs' of a series of 2-substituted 4,6-diamino-1,3,5-triazines, **3**.[6] The values of pK_{b1}, pK_{b2}, and pK_{b3} were found to be 9.19, 11.74, and 12.1, respectively (R = $-CH_3$). They predicted that the first protonation did not take place at the amino groups but instead occurred at either the 1- or the 3-nitrogen of the triazine ring. They also predicted that, with respect to the induced positive charges at the amino groups after the first protonation, it was probable that the second protonation would take place at a remaining ring nitrogen. Likewise, the third protonation would also take place at the remaining ring nitrogen.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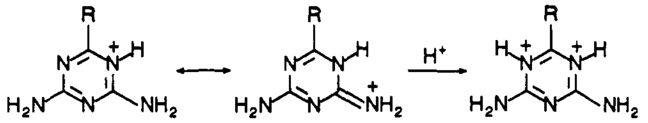
R = $-CH_3$, -H, -Ph



In this paper, the tautomerization of ammeline and the first, second, and third protonations of ammeline are studied by ab initio calculations. The acidity of ammeline and the properties of the anion of ammeline, **4**, are also investigated. It is also the first time that the structures of melamine, **5**, and 2,4-diamino-1,3,5-triazine, **6**, have been studied by the ab initio method.

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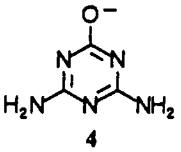

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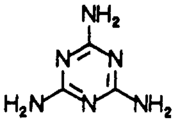

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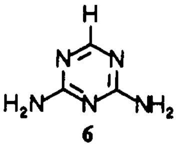

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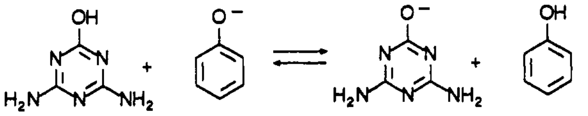
Method of Calculations

The geometries of melamine, ammeline, and 2,4-diamino-1,3,5-triazine were completely optimized at the Hartree–Fock level using the program TEXAS.[7] This program solves the Roothaan–Hall equations using a basis set of contracted Gaussian functions, and the geometries are determined by the force relaxation method of Pulay.[8] The standard split-valence basis sets, 4-21G*[9] and 6-31G**[10], were used. They include d polarized functions on all heavy atoms and p functions on hydrogens. The minimal STO-3G[11] basis set was also used.

The calculations on the anion of ammeline were conducted using the 6-31G** basis set. It is known that calculations of the intrinsic properties (e.g., electron affinity) of molecular anions at the SCF level are inaccurate since the correlation energy in the anion is generally considerably greater than that of the neutral molecule.[12] Similar difficulties are encountered when determining energy changes for reactions involving neutral species with differing numbers of electron pairs. Therefore, a reliable theoretical prediction of electron affinities requires some means of taking into account electron correlation. However, the equilibrium geometry can be predicted within the Hartree–Fock framework. The correlation energy does not change significantly with small changes in bond length and bond angle in the vicinity of the potential minimum on the Hartee–Fock surface. To circumvent these difficulties the acidity of ammeline was evaluated by calculating the heat of the isodesmic proton transfer reaction[13] (eq 1) between the ammeline and phenol anion.

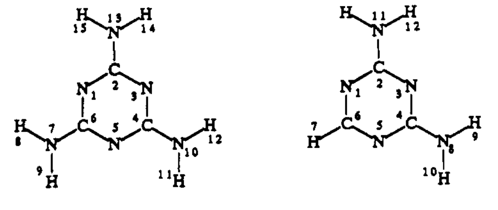


(1)

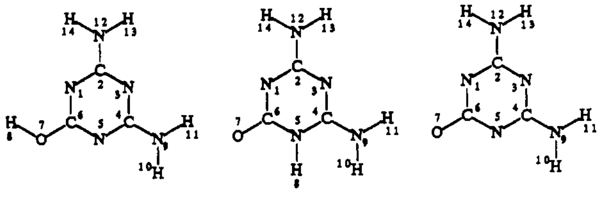
The same procedures can also be used for studying closed shell cations.[14] The geometries of mono-, di-, and triprotonated ammeline were fully optimized using STO-3G basis set. Their SCF energies of the various nitrogen-protonated isomers of ammeline were compared.

The ionization potentials of melamine, ammeline, and 2,4-diamino-1,3,5-triazine (Tables I–III) were estimated according to Koopmans' theorem[15] where the first ionization potential is equal to the negative value of the highest occupied orbital energy.

Results and Discussion



Melamine 2,4-Diamino-1,3,5-triazine



Ammeline Tautomer 1 Ammeline Tautomer 2 Ammeline Anion 4

Figure 1. Labeling of structures.

Table I. Ab Initio Calculations on Melamine. Summary of Optimized Geometries, Ionization Potentials, and Total Energies for Different Basis Sets

parameters[a]	exptl[b]	6-31G**	4-21G*	STO-3G
N_1–C_2	1.334	1.327	1.324	1.359
C_2–N_3	1.333	1.327	1.324	1.359
N_3–C_4	1.342	1.327	1.324	1.360
C_4–N_5	1.336	1.327	1.324	1.360
N_5–C_6	1.340	1.327	1.324	1.360
C_6–N_1	1.343	1.327	1.324	1.360
C_2–N_{13}	1.357	1.342	1.354	1.416
N_{13}–$H_{14,15}$	0.85, 0.78	0.991	1.001	1.024
C_4–N_{10}	1.334	1.341	1.353	1.414
N_{10}–$H_{11,12}$	0.83, 0.73	0.991	1.000	1.024
$\angle N_1C_2N_3$		126.1	126.6	127.6
$\angle C_2N_3C_4$	115.0	113.9	113.4	112.3
$\angle N_3C_5N_5$		126.1	126.6	127.6
$\angle C_4N_5C_6$	115.3	113.9	113.4	112.3
$\angle N_{13}C_2N_1$	116.7	117.0	116.7	116.1
$\angle H_{14}N_{13}C_2$	114.0	119.0	115.5	112.3
$\angle H_{15}N_{13}H_{14}$	117.3	120.6	116.7	112.3
$\angle N_{10}C_4N_3$	117.5	117.0	116.7	116.1
$\angle H_{11}N_{10}C_4$	116.4	119.1	115.6	112.6
$\angle H_{12}N_{10}H_{11}$	122.9	120.8	115.6	112.5
δ_{13}	8.43	12.2	34.9	47.06
δ_{10}	4.03, 3.18	9.9	33.7	46.3
θ_{13}		0.49	1.47	2.60
θ_{10}		0.36	1.16	2.20
tors. $N_3C_2N_1C_6$		0	0.67	1.1
IP (eV)		9.54	9.39	7.80
TE (+443 au)		−0.884 028	0.074 255	4.856 214

[a] Bond lengths in Å and angles in deg. [b] X-ray crystallographic data.[16]

I. Optimized Geometries. Ab initio calculations on aniline[16] employing the minimal STO-3G and 4-21G*[17] basis sets exaggerate the non-planarity of the amino group compared to the experimental data. Only calculations using the 6-31G** basis set[16] gave ring and amino group geometries for aniline very close to the experimental[18] results. The same criteria were observed in the calculations on melamine, ammeline, and 2,4-diamino-1,3,5-triazine. Their detailed structure features are discussed in following sections, and the numbering system used in the tables and text is shown in Figure 1. The discussion below is based on our best results. Unless stated otherwise, these results were obtained with the 6-31G** basis set.

Melamine. The calculated geometrical parameters obtained using each of the different basis sets are listed in Table I. The experimental crystallographic data[19] are also included in the table for comparison. An experimental gas-phase geometry of melamine has never been reported.

The predicted optimized equilibrium geometry of melamine has a plane of symmetry perpendicular to the

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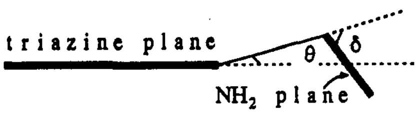

Figure 2. Definition of out of plane angles δ and θ.

triazine ring and bisecting one of its amino groups ($\angle H_{14}N_{13}H_{15}$). The triazine ring was very slightly twisted using the STO-3G and 4-21G* basis sets and essentially planar using the 6-31G** basis set. At all levels of calculations presented here, the amino groups of melamine are nonplanar (one up, and two down). The out of plane angles, which the ring carbon to amino nitrogen bonds make with NH_2 planes (e.g., angle δ in Figure 2) were 12.2° (one up) and 9.9° (two down). The corresponding crystallographic values[17] were 8.43° and 4.03°. Though the error (~50%) appears large, the overall amino group conformations of melamine are predicted quite well.

There are reasons that could account for the differences between the calculated and crystallographic values of δ. First, the crystallographic values may not be good candidates for comparison with calculated values because calculated geometries refer to the gas phase. Hydrogen bonding and packing of the molecules in the crystal may exert a serious influence on the conformation of the amino groups. Second, the use of limited basis sets and the neglect of electron correlation may of course cause errors in the geometries. However, on the basis of our previous calculations on aniline,[16] the calculated equilibrium geometry of melamine predicted by ab initio calculations (6-31G** level) is expected to be close to its gas-phase geometry.

The amino group nitrogens of melamine lie slightly out of the triazine ring plane (σ = 0.36° and 0.49° for N_{10}–C_4 and N_{13}–C_2, respectively). The calculated bond lengths of the C–N bonds in the ring (1.327 Å) were all equal and were shorter than C–N bond lengths in pyridine (1.338 Å, via microwave spectra[18]). This is consistent with aromaticity (delocalization) which accounts for the high thermal stability of the triazine ring. The calculated C–N bond lengths (1.342 Å) between the amino groups and triazine ring were shorter than the C–N bond length in aniline (1.402 Å, via microwave spectra,[20] and 1.394 Å, calculated using the 6-31G** basis set[16]). This length is also shorter than the C–N bond length in formamide (1.376 Å, via microwave spectra[21]).

The triazine ring of melamine was severely distorted from an ideal hexagon. The ring N–C–N angles were calculated to be larger (126.1°) than the ring C–N–C angles (113.9°).

2,4-Diamino-1,3,5-triazine. Table II lists the calculated geometrical features of 2,4-diamino-1,3,5-triazine using the three different basis sets. The optimized geometry (6-31G** basis) exhibited C_{2v} symmetry. The molecule was planar. Melamine has three lone pairs of electrons on its three amino group nitrogens versus only two for 2,4-diamino-1,3,5-triazine. Therefore, the magnitude of the π-delocalization of each amino group into the electron-deficient triazine ring in 2,4-diamino-1,3,5-triazine was expected to be larger than that found in melamine. This is consistent with the finding that the amino groups on 2,4-diamino-1,3,5-triazine were planar instead of the slightly pyramidal geometry found in melamine. As anticipated, the C–N bond lengths between the ring and amino groups were shorter (1.338 Å) in 2,4-diamino-1,3,5-triazine than those of melamine (1.342 Å).

Table II. Ab Initio Calculations on 2,4-Diamino-1,3,5-triazine. Optimized Geometries, Ionization Potentials, and Total Energies Using Different Basis Sets

parameters[a]	6-31G**	4-21G*	STO-3G
N_1–C_2	1.336	1.333	1.365
N_1–C_6	1.313	1.312	1.349
C_2–N_3	1.324	1.322	1.357
C_6–H_7	1.077	1.081	1.092
C_2–N_{11}	1.338	1.349	1.414
N_{11}–$H_{12,13}$	0.991	1.000	1.025
$\angle N_1C_6N_5$	127.3	127.8	127.9
$\angle C_2N_1C_6$	113.6	113.1	112.6
$\angle N_3C_2N_1$	125.4	126.0	127.0
$\angle C_4N_3C_2$	114.5	114.0	112.8
$\angle H_7C_6N_1$	116.3	116.1	116.1
$\angle N_{11}C_2N_1$	117.0	116.8	116.4
$\angle H_{12}N_{11}C_2$	119.3	116.1	112.4
$\angle H_{13}N_{11}C_2$	119.6	116.4	112.6
$\angle H_{13}N_{11}H_{12}$	121.1	117.4	112.5
tors. $N_3C_2N_1C_6$	0	0.83	1.29
δ_{11}	0	31.6	46.4
θ_{11}	0	1.3	2.56
IP (eV)	9.56	9.36	7.82
TE (+388 au)	−0.823 067	−0.122 682	4.191 907

[a] Bond lengths in Å and angles in deg.

Ammeline. The bond lengths and angles for the optimized geometries of both the hydroxy (**1**) and carbonyl (**2**) tautomers of ammeline calculated using different basis sets are summarized in Table III. Both the STO-3G and 4-21G* basis sets predicted significantly nonplanar geometries (of rings and amino groups) for both tautomers of ammeline while the 6-31G** basis set predicted planar geometries. Also, the amino groups were coplanar with the ring at this level. Hydroxy tautomer, **1**, was 4.82 kcal/mol more stable than carbonyl tautomer, **2**.

The C–N ring bond lengths for the hydroxy tautomer, **1**, were slightly different. The presence of H–O bond makes these bonds nonequivalent. The C_6–N_1 and C_6–N_5 bond lengths were a little shorter than the lengths of the other ring bonds which can be explained by the strong inductive effect of the oxygen. The calculated C–O bond length of ammeline (1.316 Å) was shorter than that in phenol (1.351 Å at the 6-31G** level calculated in this work and 1.364 Å was determined via microwave spectroscopy[22]). This should be expected due to the more electron-deficient character of the triazine ring relative to the benzene ring. The C–O bond length of tautomer **2** was 1.195 Å, which is typical for a carbonyl bond (e.g., ~1.20 Å). The C–N bond lengths between the triazine ring and the amino groups were about the same in both tautomers.

Deprotonated Ammeline. The calculated structure of anion **4** was very interesting. The RHF-SCF 6-31G** level used was considered essential for calculations on organic anions.[12] As shown in Table III, the optimized geometry has C_2 symmetry. The C_2 axis passes through the O, C_6, and N_3. A major difference between the anion and neutral ammeline is that the amino groups are no longer planar in the anion. The out of plane angle of the amino groups (the angle the C–N bond makes with NH_2 plane), δ, was predicted to be 43.9°. This angle is very

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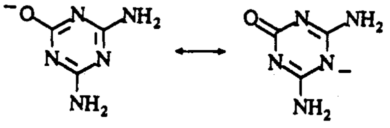
Table III. Ab Initio Calculations on Ammeline and Its Anion. Summary of Optimized Geometries, Ionization Potentials, and Total Energies Using Different Basis Sets

	6-31G**					STO-3G	
parameters[a]	hydroxy tautomer 1	carbonyl tautomer 2	carbonyl tautomer 11	anion	4-21G* hydroxy tautomer 1	hydroxy tautomer 1	carbonyl tautomer 2
N_1-C_2	1.331	1.306	1.264	1.297	1.328	1.362	1.306
N_1-C_6	1.311	1.348	1.402	1.384	1.310	1.355	1.439
N_3-C_2	1.327	1.358	1.377	1.335	1.325	1.361	1.430
N_3-C_4	1.324	1.296	1.377	1.335	1.322	1.358	1.308
N_5-C_4	1.332	1.342	1.264	1.297	1.329	1.361	1.387
N_5-C_6	1.319	1.417	1.402	1.384	1.317	1.357	1.450
$O-C_6$	1.316	1.195	1.187	1.213	1.320	1.374	1.218
O–H (N–H)	0.946	(0.992)	(0.995)		0.964	1.990	(1.021)
N_9-C_4	1.337	1.338	1.362	1.385	1.349	1.412	1.424
$N_{12}-C_2$	1.336	1.336	1.362	1.385	1.347	1.411	1.418
$N_9-H_{10,11}$	0.991	0.992	0.996	0.995	1.000	1.024	1.028
$N_{12}-H_{13,14}$	0.991	0.991	0.996	0.995	1.000	1.024	1.025
$\angle C_6N_1C_2$	113.4	118.2	118.9	111.6	113.0	111.8	116.4
$\angle N_1C_2N_3$	125.9	127.9	123.2	128.2	126.4	127.7	130.4
$\angle C_2N_3C_4$	114.2	114.7	116.6	111.4	113.6	112.6	112.5
$\angle N_3C_4N_5$	125.5	121.9	123.2	128.2	126.0	127.2	124.1
$\angle C_4N_5C_6$	113.8	121.9	118.9	116.6	113.3	112.3	121.4
$\angle N_5C_6N_1$	127.2	115.4	118.8	119.0	127.6	128.3	115.0
$\angle H_8O_7C_6$	108.2				106.2	103.9	
$\angle N_1C_6O_7$	116.1	127.7	120.6	120.5	115.9	115.3	125.0
$\angle N_1C_2N_{12}$	116.8	117.8	121.9	116.9	116.6	116.1	117.6
$\angle N_3C_4N_9$	117.5	119.6	114.8	114.8	117.2	116.3	119.8
$\angle C_2N_{12}H_{14}$	119.6	119.8	112.9	112.4	116.6	113.0	112.2
$\angle C_2N_{12}H_{13}$	119.3	118.9	117.4	113.1	116.4	112.8	112.1
$\angle H_{14}N_{12}H_{13}$	121.2	121.4	114.6	115.0	117.8	113.0	112.3
$\angle C_4N_9H_{11}$	119.4	117.7	117.4	112.4	116.2	112.6	109.9
$\angle C_4N_9H_{10}$	119.6	122.6	112.9	113.1	116.3	112.8	112.4
$\angle H_{10}N_9H_{11}$	121.0	119.7	114.6	115.0	117.4	112.6	110.3
δ_9	0	0	39.2	43.9	31.8	45.9	50.9
δ_{12}	0	0	39.2	43.9	30.2	45.3	47.4
θ_9	0	0	1.33	0.72	1.3	2.5	2.2
θ_{12}	0	0	1.33	0.72	1.2	2.4	2.2
tors. $N_3C_2N_1C_6$	0	0	3.11	1.14	0.8	1.4	1.62
tors. $H_8O_7C_6N_5$	0				0	0	
tors. $H_8N_5C_4N_3$		0					173.74
IP (eV)	9.84	9.68	10.08	4.26	9.64	8.01	7.10
TE (+463 au)	−0.708 15	−0.700 47	−0.670 18	−0.128 37	0.144 27	5.334 09	5.356 26

[a] Bond lengths in Å and angles in deg.

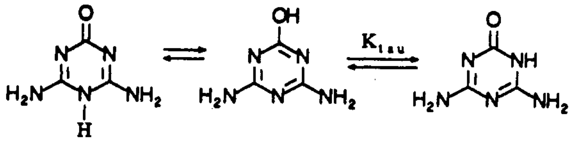
close to that of aniline.[15] The O^- function supplies substantial electron density to the ring, thereby decreasing the demand for electron density from the amino groups. Therefore, the amount of π-bond character in the H_2N-C bonds drops sharply and the amino nitrogens become pyramidal. This should lead to a large increase in the nucleophilicity of the amino groups in the anion of ammeline compared to the neutral molecule. These properties will be discussed in detail in later.

Consistent with this picture was the lengthening of the C–N bond lengths between the triazine ring and the amino groups to 1.385 Å in anion 4 compared to 1.337 Å in the neutral molecule. The C–O bond length was shortened to 1.213 Å compared to 1.316 Å in the hydroxy tautomer. In fact, the C–O length is only slightly longer in 4 than the C–O length in the carbonyl tautomer (1.195 Å). This illustrates the very strong electron donation and high π-bond order from oxygen to the ring in anion 4. The N_1-C_2 and C_4-N_5 bond lengths of 4 were much shorter than the other ring bond lengths showing the existence of a strong contribution of the quinoid-like hybrid structure 7.



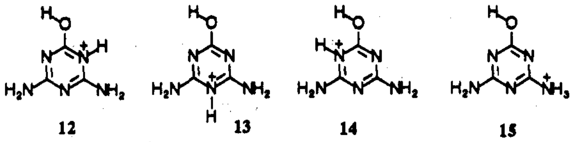
4 7

II. Structures and Properties of Ammeline. Tautomerization of Ammeline. The calculated energy of the hydroxyammeline tautomer, 1, was found to be 4.82 kcal/mol lower than that of the carbonyl tautomer, 2, and 23.3 kcal/mol lower than that of carbonyl tautomer 8. The energy change of the tautomerization equilibrium between 1 and 2 was −4.82 kcal/mol. This should be close to the free energy change ($\Delta G°$) because the entropy change of the reaction should be close to zero. Using the calculated energy change of the tautomerization as an estimate of the Gibbs free energy change ($\Delta G°$), the equilibrium constant K_{tau} is estimated to be about 2.9×10^{-4} at 25 °C. Therefore, hydroxy tautomer 1, 2-hydroxy-4,6-diamino-1,3,5-triazine, should be the dominant tautomer of ammeline in the gas phase. However, this tautomer may not necessarily represent the structure of ammeline in the solid state. Unfortunately, the crystallographic structure for ammeline is not available yet.



8 1 2

The quinoid-like carbonyl tautomer 8 was much less stable than tautomers 1 and 2 (by 23.8 and 19.0 kcal/mol,



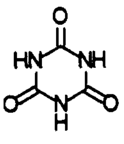
	12	13	14	15
STO-3G	-27.51	-20.92	-17.35	0
4-21G*	-25.72	-18.74	--	0

(ΔE in kcal/mole)

Figure 3. Monoprotonation of ammeline.

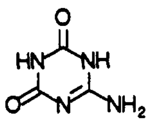
respectively). Steric repulsion between the amino group hydrogens and the hydrogen attached to the ring nitrogen caused the molecule to be nonplanar. The amino groups each exhibit a 39° out of plane angle. The hydrogen on the ring nitrogen is bent 22° out of the ring plane. The partial loss of aromaticity and the steric deformations increased the energy of tautomer 8. The C–O length of 8 is shorter (1.187 Å) than that in 2 (1.195 Å) and much shorter than that of 1 (1.316 Å). The exocyclic C–N bond lengths (1.362 Å) are longer than those in 1 and 2 (1.336–1.338 Å). The lengths of the N_1–C_2 and C_4–N_5 ring bonds are much shorter (1.264 Å) than the rest of the ring bond lengths. All these changes indicate the localization of the π-bonds in tautomer 8.

In the *8th Collective Index of Chemical Abstracts*, the IUPAC name of ammeline was changed from 4,6-diamino-*s*-triazin-2-ol to 4,6-diamino-*s*-triazin-2(1*H*)-one. This name change indicated that the amide-like (carbonyl) tautomer 2 was favored as the structure. Acceptance of this name may have been supported by the structures of cyanuric acid, 9, and ammelide, 10. However, the chemical properties of ammeline are totally different than those of cyanuric acid and ammelide. For example, it is known that cyanuric acid,[23] 9, and ammelide,[24] 10, condense with formaldehyde only at the ring nitrogens. In contrast, the reaction of ammeline with formaldehyde takes place only at the amino groups. Furthermore, the isolated hydroxymethylated products from ammeline contain only one hydroxymethyl group at each NH_2.[18,20]



9

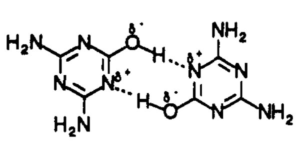
Cyanuric Acid



10

Ammelide

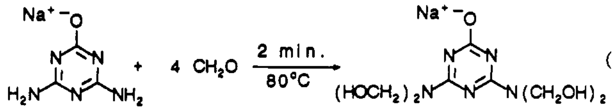
A careful search of the literature revealed that there is little experimental evidence that could support the amide-like tautomeric structure, 2, for ammeline. One possible exception is the IR spectra which showed an absorption at 1700–1715 cm^{-1} [25] attributed to a carbonyl stretch. However, in the same article,[25] the C=N$^+$ stretchings were shown also to fall in the 1700–1720 cm^{-1} region for the salts of several diamino-1,3,5-triazine derivatives. Since the hydroxy group of ammeline, 1, is quite acidic (this will be further discussed in later section), it is possible that the acidic hydroxy group forms strong hydrogen bonds with the basic ring nitrogens (structure 11). The partial positive charge on the nitrogen may then cause the absorption of the C=N stretching band to shift to that of the C=N$^+$ regions where it might be confused with a carbonyl stretch. The strong hydrogen bonds also contribute to the low solubility of ammeline in general.



11

Acidity of Ammeline. The geometric features of the anion of ammeline have already been discussed. A significant result is that the amino groups of this anion are pyramidal with an out of plane angle similar to that of aniline,[16] whereas the geometry of ammeline is planar. This suggests the nucleophilicity of the amino groups of ammeline should undergo a large increase in strongly basic media. In fact, we have now demonstrated this principle in the nucleophilic addition to formaldehyde.

For example, it is known that all four hydrogen atoms on the amino groups of ammeline could be substituted at pH 9–10 in the presence of a large excess of formaldehyde at 80 °C after 6 h (0.2 g of ammeline in 25 mL of 37% formaldehyde, formaldehyde/ammeline mole ratio > 150).[26] However, when 1 equiv of NaOH is added to ammeline (pH ~11), then 4 mol of formaldehyde reacted with ammeline to form the tetrakis-*N*-(hydroxymethyl)-ammeline in 2 min at the same temperature.[27]



(2)

Evaluations of the acidity of organic compounds by direct calculations of proton affinities was demonstrated to give serious errors.[12] A practical method to study relative acidities involves calculating the energy change of the isodesmic proton transfer reactions.[28] We calculated the energy change of the proton transfer reaction, eq 1, between ammeline and phenol to compare the relative acidity of ammeline to phenol. The energy change in equation 1 was −10.11 kcal/mol. Thus, ammeline was substantially more acidic than phenol. This corresponds to the observation that ammeline dissolves in sodium carbonate solution, whereas the phenol dissolves in sodium hydroxide solution but is precipitated upon purging the solution with CO_2.

Protonation of Ammeline. Figure 3 illustrates the different positions where protonation might occur on ammeline. The relative energies calculated for each of these species are also listed below each of the structures. The energies of all three ring-protonated species are much lower than the energies of the species protonated at the amino group. The energy of the most stable species, 12, is 25.72 kcal/mol (4-21G*) lower than the species protonated at the amino group, 15. This calculation lends strong support to the prediction that protonation of ammeline occurs first at the 1- or 5-position.

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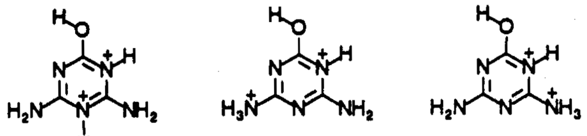
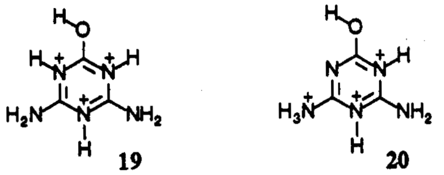


16 **17** **18**

-9.8 0 +12.08

(ΔE in kcal/mole using STO-3G basis set)

Di-protonation of Ammeline



19 **20**

-14.22 0

(ΔE in kcal/mole using STO-3G basis set)

Triprotonation of Ammeline

Figure 4. Multiple protonation of ammeline.

As stated earlier, calculations on ammeline at the STO-3G and 4-21G* levels predicted nonplanar geometries for the amino groups. However, the calculated optimized geometries of the protonated ammelines all had planar amino groups using both the STO-3G and 4-21G* basis sets. Protonation will result in a more electron-deficient triazine ring. Therefore, the amino nitrogen must contribute more electron density to the conjugated system via back π-donation.

Valence bond analysis favors the prediction that the second protonation of ammeline would also occur on a ring nitrogen. This prediction is in agreement with our calculations. The energy of the 1,5-diprotonated ammeline, **16**, is 9.8 kcal/mol lower than the ring/amino diprotonated species, **17**, using the STO-3G basis set. Although the energy difference is not as large as it is in the monoprotonated species, a 9.8 kcal/mol difference is significant. The energy difference between **17** and **18** is believed to be caused by the repulsion of two positive charges which are closer together in **18** than in **17**.

The calculated results indicated that the third proton would also add to the remaining ring nitrogen. Structure **19** was 14.22 kcal/mol more stable than **20** (STO-3G basis set).

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