Quantum Chemical Study of the Structure and Thermochemistry of the Five-Membered Nitrogen-Containing Heterocycles and Their Anions and Radicals

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The nitrogen-containing heterocycles are of interest as high-energy-density materials for use as propellants and explosives, while the pyrolysis of these compounds is also important in understanding the evolution of unwanted NO and NO_2 (NO_x) from organic fuels such as coal and biomass. We have used ab initio and density functional methods to study the molecular structures and thermochemical properties of the five-membered nitrogen-containing heterocycles and their anions and radicals corresponding to respective heterolytic and homolytic loss of a hydrogen atom from either a nitrogen or carbon site. Many of these thermochemical properties have not previously been measured, especially for the heterocycles containing three and four nitrogen atoms. Using the theoretical methods CBS-APNO, G3, and G3B3, we calculate enthalpies of formation of 26.5, 42.4, 31.9, 63.7, 46.8, 81.0, and 79.0 kcal mol^{-1} for pyrrole, pyrazole, imidazole, 1,2,3-triazole, 1,2,4-triazole, 1*H*-tetrazole, and 2*H*-tetrazole. A correlation is developed between the number of nitrogen atoms in a heterocycle and its enthalpy, and we extrapolate this relationship to predict the enthalpy of formation of pentazole. N−H BDEs in the heterocycles typically increase with the number of nitrogen atoms in the molecule, while C−H BDEs are similar in all of the studied heterocycles, at around 120 kcal mol^{-1}. In all cases the N−H BDEs are weaker than the C−H BDEs, suggesting abstraction of the N−H hydrogen atom is more likely. Deprotonation enthalpies and free energies reveal that the N−H protons become more acidic with increasing number of nitrogen atoms in the heterocycle. C−H protons are less acidic than N−H protons by ca. 49 kcal mol^{-1}, or ca. 35 kcal mol^{-1} when adjacent to the NH group. Trends in N−H and C−H acidities can be qualitatively explained by electrostatic effects and electron affinities. From its use as a reference species in our calculations, we identify that the experimental enthalpy of pyrimidine (1,3-diazine) may be in error by ca. 1−3 kcal mol^{-1}, and we recommend an enthalpy of formation of 44.8 ± 1.0 kcal mol^{-1}.

Introduction

There is significant interest in the high-energy-density five-membered nitrogen-containing heterocycles, due to their possible applications as propellants and explosives. There is particular interest in the triazoles (cyclo-$C_2N_3H_3$) and tetrazoles (cyclo-CN_4H_2), along with their various salts and substituted derivatives.[1] The one and two nitrogen atom heterocycles pyrrole (cyclo-C_4NH_4) and pyrazole and imidazole (cyclo-$C_3N_2H_3$) are also important, as they aid in the understanding of their more nitrogen-rich analogues. Salts of the cyclic pentazolide anion (cyclo-N_5^-) have also been synthesized recently,[2] and these compounds hold promise as highly energy dense materials. Again, understanding the properties of pentazolide's five-membered heterocyclic analogues helps provide insight into the behavior of pentazolide itself, as well as its theorized parent molecule pentazole (cyclo-N_5H).

The high-temperature reactions of five- and six-membered nitrogen-containing heterocycles are also of interest in atmospheric and combustion chemistry, due to the role of these compounds in the production of the pollutants NO and NO_2 (NO_x) during combustion processes.[3] Heterocyclic nitrogen-containing functional groups are prominent in organic fuels such as coal and biomass; these fuels can contain significant nitrogen, and in most coals this nitrogen is predominantly present in the pyrrolic form.[4] Accordingly, understanding the reaction pathways of these compounds is important in constructing kinetic models which accurately predict NO_x evolution rates from the pyrolysis and combustion of coal and biomass, as well as from other fuels. The reaction kinetics of pyrrole and pyridine in thermal systems have been thoroughly examined experimentally,[5] though these systems have not been so extensively studied theoretically,[6] and there has been little experimental or theoretical work on other nitrogen-containing heterocycles. For pyrrole and pyridine oxidation, major nitrogen-containing reaction products identified in experiments include cyanoacetylene, hydrogen cyanide, NO, and N_2.[5] Unimolecular C−H bond fission has been proposed as an important initial reaction step in the combustion of pyridine,[5c,e] and these bond energies are needed to evaluate the kinetics of hydrogen atom abstraction in the nitrogen-containing heterocycles.

Recently, bond dissociation energies (BDEs) and acidities of the five-membered heterocycles containing one and two nitrogen atoms have been obtained using photoelectron spectroscopy.[7−9] N−H BDEs for pyrazole and imidazole were determined to be 108.0 ± 0.4 and 96.5 ± 0.6 kcal mol^{-1}, respectively, while C−H BDEs were estimated at 121 ± 4 and 119 ± 4 kcal mol^{-1}. Previous studies have found the N−H BDE in pyrrole to be 96.6 kcal mol^{-1},[10] 99 ± 6 kcal mol^{-1},[11] 88 ± 2 kcal mol^{-1},[12] and 92.6 ± 1 kcal mol^{-1},[13] while the pyrrole C−H BDE has

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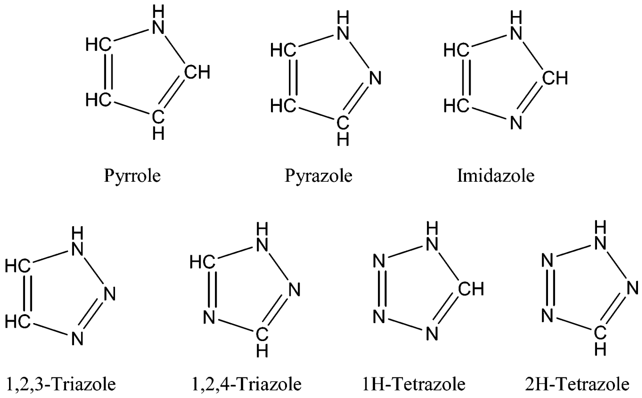
SCHEME 1: Five-Membered Nitrogen-Containing Heterocycles



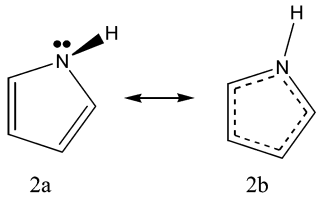
been measured as 112.5 $\pm$ 1 kcal mol^{-1}.[12] Scott et al.[14] measured the enthalpy of formation of pyrrole as 25.88 $\pm$ 0.12 kcal mol^{-1}. The enthalpy of formation of pyrazole has previously been found to be 42.9 $\pm$ 0.2 kcal mol^{-1} [15] and 43.3 $\pm$ 2.1 kcal mol^{-1},[16] while that of imidazole has been measured as 33.29 $\pm$ 0.45 kcal mol^{-1},[15] 31.8 $\pm$ 0.1 kcal mol^{-1},[16] and 30.6 $\pm$ 1.8 kcal mol^{-1}.[17] The higher nitrogen content five-membered heterocycles are less well-studied, although the enthalpy of formation of 1,2,4-triazole has been measured as 46.1 $\pm$ 0.2 kcal mol^{-1} [15] and 46.3 $\pm$ 0.45 kcal mol^{-1},[18] while that of 1*H*-tetrazole has been found to be 78.1 $\pm$ 0.7 kcal mol^{-1} [19] and 76.6 $\pm$ 0.7 kcal mol^{-1}.[20] To our knowledge, neither N−H nor C−H BDEs or acidities have been measured for any of the five-membered heterocycles containing three or four nitrogen atoms. The above results suggest that there is value in accurate determination of the formation enthalpies, bond energies, and proton acidities of the five-membered nitrogen-containing heterocycles, especially those with three and four nitrogen atoms. These data would allow calibration of the computation methods for use on extensions of these unsaturated nitrogen-containing heterocyclic ring systems and resolve the discrepancies noted above, while also providing information on the relative stability of these compounds with increased nitrogen substitution in the rings.

The five-membered nitrogen-containing heterocycles are an important class of molecules. Knowledge of their thermochemistry and the N−H and C−H bond energies and acidities is of value for energetic considerations and for construction of kinetic mechanisms to model their combustion, oxidation, and propulsion processes. The relative instability and highly exothermic combustion of many of these nitrogen-containing species lead to difficulties in determining their thermochemistry by experiment, and ab initio calculations are therefore well-suited to studying these molecules. We have examined the structure and thermochemistry of the five-membered nitrogen-containing heterocycles pyrrole, imidazole, pyrazole, 1,2,3-triazole, 1,2,4-triazole, 1*H*-tetrazole, and 2*H*-tetrazole using quantum chemical methods. These species are illustrated in Scheme 1. The radicals and anions corresponding to the heterolytic and homolytic loss of a hydrogen atom are also studied.

Computational Methods

Calculations were performed with the Gaussian 03 suite of programs.[21] The CBS-APNO,[22] G3,[23] and G3B3[24] composite theoretical methods were used to study each of the nitrogen-containing heterocycles and their radicals and anions. The CBS-APNO, G3, and G3B3 methods provide average errors of 0.7, 0.9, and 1.0 kcal mol^{-1} with the G2 test set of small molecules. In this study we are examining larger molecules (five heavy atoms), and computational errors would be expected to be somewhat greater due to systematic errors and spin contamination in the radical species. However, errors in the range of 1−2 kcal mol^{-1} are realistic.

SCHEME 2: Pyrrole Resonance Structures

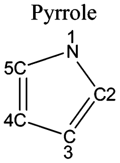
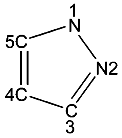
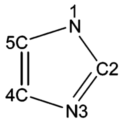
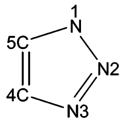
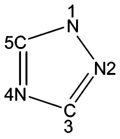
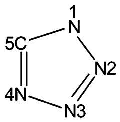
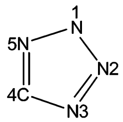


The G3 and CBS-APNO methods both involve an initial Hartree−Fock (HF) geometry optimization and frequency calculation with the 6-31G(d) and 6-311G(d,p) basis sets, respectively. These calculations are followed by a further geometry optimization using a correlated theoretical method with the same basis set: second-order Møller-Plesset (MP2) perturbation theory for G3 and quadratic configuration interaction theory with single and double substitutions (QCISD) for CBS-APNO. The G3B3 method makes use of the fact that the B3LYP DFT method provides a greater account of electron correlation than HF theory, while being more computationally efficient than the MP2 method, and performs a single geometry optimization and frequency calculation at the B3LYP/6-31G(d) level. Of the three theoretical methods employed in this study, the CBS-APNO QCISD/6-311G(d,p) calculation represents the highest level geometry optimization, and these geometries are therefore reported here when the molecular structures are analyzed. For the 1,2,3-triazol-1-yl and 1,2,4-triazol-1-yl radicals, the G3 method's MP2/6-31G(d) geometry optimization step did not converge, and therefore only G3B3 and CBS-APNO results are presented for these radicals. The average thermochemical properties reported in this study are weighted averages, with 25% G3, 25% G3B3, and 50% CBS-APNO, so as to similarly weigh the G3-type and the CBS-type calculations.

Enthalpies of Formation. Standard enthalpies of formation ($\Delta_f H°_{298}$) are calculated using isodesmic and/or atomization work reactions. Atomization reactions make use of the enthalpies of formation of the atomic elements in calculating enthalpies of formation, but there is no cancellation of bond energy across the work reaction, leading to relatively large systematic bonding errors. Isodesmic reactions feature the same number and type of each bond on both sides of the reaction and often lead to cancellation of errors resulting from the bond environments. The use of the same number of radical electrons and internal rotors on both sides of the reaction can yield further cancellation of errors due to the effects of spin contamination and hindered internal rotation. The disadvantage in use of isodesmic reaction analysis is the need for accurate enthalpies of formation for the reference species in the reaction.

The use of isodesmic reactions to calculate thermodynamic properties with computational methods such as G3 and CBS-APNO has been shown to reduce computational errors from around 1 to around 0.5 kcal mol^{-1} or below, but only when accurate reference enthalpies of formation are available.[25] Experimental enthalpies of formation have been precisely measured for many hydrocarbons and oxyhydrocarbons; however, there are not as many accurate measurements for nitrogen-containing organic molecules. We make use of the apparently accurate thermochemical property data of the six-membered nitrogen-containing heterocycles pyridine, pyridazine, and pyrimidine to construct isodesmic work reactions for pyrrole,

TABLE 1: Bond Lengths (Å) for Pyrrole, Pyrazole, Imidazole, 1,2,3-Triazole, 1,2,4-Triazole, 1*H*-Tetrazole, and 2*H*-Tetrazole at the QCISD/6-311G(d,p) Level of Theory

Pyrrole		Pyrazole		Imidazole		1,2,3-Triazole		1,2,4-Triazole		1H-Tetrazole		2H-Tetrazole	
													
N1-C2	1.37596	N1-N2	1.34761	N1-C2	1.36637	N1-N2	1.34482	N1-N2	1.35604	N1-N2	1.34994	N1-N2	1.32218
N1-C5	1.37596	N1-C5	1.35925	N1-C5	1.38214	N1-C5	1.35857	N1-C5	1.35065	N1-C5	1.34813	N1-N5	1.32807
C2-C3	1.37901	N2-C3	1.33011	C2-N3	1.31321	N2-N3	1.29764	N2-C3	1.32218	N2-N3	1.28419	N2-N3	1.30563
C3-C4	1.43260	C3-C4	1.42057	N3-C4	1.38456	N3-C4	1.37073	C3-N4	1.36958	N3-N4	1.36874	N3-C4	1.35991
C4-C5	1.37901	C4-C5	1.38210	C4-C5	1.37238	C4-C5	1.37594	N4-C5	1.31959	N4-C5	1.31225	C4-N5	1.32603
N1-H	1.00498	N1-H	1.00567	N1-H	1.00600	N1-H	1.00711	N1-H	1.00648	N1-H	1.00706	N1-H	1.00839
C2-H	1.08080	C3-H	1.08205	C2-H	1.08191	C4-H	1.07916	C3-H	1.08089	C5-H	1.07919	C4-H	1.07877
C3-H	1.08152	C4-H	1.07985	C4-H	1.08105	C5-H	1.07885	C5-H	1.08145	-	-	-	-
C4-H	1.08152	C5-H	1.08093	C5-H	1.07959	-	-	-	-	-	-	-	-
C5-H	1.08080	-	-	-	-	-	-	-	-	-	-	-	-

pyrazole, and imidazole. For the remaining heterocycles, we utilize atomization reactions to calculate enthalpies of formation. The formation enthalpies of pyrrole, pyrazole, and imidazole are also determined through atomization calculations to evaluate our choice of isodesmic work reactions.

Bond Dissociation Energies. The bond dissociation energy corresponding to loss of a hydrogen atom is equivalent to the enthalpy change across a reaction of the type RH → $R^\bullet + H^\bullet$. The extent of error cancellation in a reaction such as this is considerably larger than in an atomization reaction, as there is only one bond being broken. However, there are still significant systematic errors due to the relatively large reaction enthalpy (typically 90−100 kcal mol^{-1} or greater for N−H and C−H bonds) and the effects of hyperconjugation and spin contamination in the radical species. As with calculating enthalpies of formation, significant error reduction can be obtained by using isodesmic work reactions for the bond energies. In this study, we use the well-known dissociation energies of the NH_2−H and CH_2═CH−H bonds in constructing isodesmic work reactions, according to the procedure described by da Silva et al.[25a] The bond energies in NH_3 and $CH_2{=}CH_2$ should be similar to those in the heterocycles that we are studying, although there will be some differences due to aromaticity in the parent molecules and hyperconjugation of the radical σ electrons. For the N−H bond energy in pyrrole (cyclo-C_4H_4NH), eq 1 is used as a work reaction; analogous reactions are used for the N−H and C−H bonds in the other heterocycles. The reaction enthalpy for eq 1 is calculated according to eq 2, and this is used in conjunction with the BDE of the reference species to calculate the pyrrole N−H BDE according to eq 3.

$$\text{cyclo-C}_4\text{H}_4\text{N{-}H} + \text{NH}_2^{\bullet} \rightarrow \text{cyclo-C}_4\text{H}_4\text{N}^{\bullet} + \text{NH}_2\text{{-}H} \quad (1)$$

$$\Delta_{\text{rxn}}H^\circ_{298}(1) = \Delta_\text{f}H^\circ_{298}(\text{cyclo-C}_4\text{H}_4\text{N}^\bullet) + \Delta_\text{f}H^\circ_{298}(\text{NH}_3) - \Delta_\text{f}H^\circ_{298}(\text{cyclo-C}_4\text{H}_4\text{NH}) - \Delta_\text{f}H^\circ_{298}(\text{NH}_2^\bullet) \quad (2)$$

$$\text{BDE(cyclo-C}_4\text{H}_4\text{N{-}H)} = \Delta_{\text{rxn}}H^\circ_{298}(1) + \text{BDE(NH}_2\text{{-}H)} \quad (3)$$

Results and Discussion

Molecular Structures, Entropies, and Heat Capacities. The nitrogen-containing heterocycles considered in this study will undergo resonance stabilization by delocalization of the nitrogen atom electron lone pair(s). Scheme 2 shows the resonance structures available to pyrrole. In structure **2a** pyrrole assumes a cyclopentadiene-type geometry, with a pyramidal nitrogen. In structure **2b** the electron lone pair on the nitrogen atom becomes delocalized into the ring, yielding a planar aromatic structure. Bond lengths for the seven heterocycles being considered in this study, optimized at the QCISD/6-311G(d,p) level of theory, are given in Table 1. All of the heterocycles are predicted to be planar, indicating that the resonantly stabilized structure is favored over the pyramidal cyclopentadiene-type structure.

Bond lengths for each of the radicals and anions corresponding to hydrogen loss are provided in the Supporting Information at the QCISD/6-311G(d,p) level. Table 2 shows the C−C, C−N, and N−N bond length changes resulting from homolytic loss of a hydrogen atom from the C−H and N−H bonds in the heterocycles. The C−H and N−H bond lengths remain essentially the same in all cases. Table 2 illustrates that removal of a hydrogen from a carbon atom results in relatively little change to the molecular geometry, with the majority of bonds changing by 0.1 Å or less. This indicates that the radical electron remains localized (predominantly) on the carbon atom, with relatively little hyperconjugation. Homolytic loss of H from nitrogen, however, is found to result in larger structural change, reflecting the multivalent nature of the nitrogen atom. Bond length changes corresponding to heterolytic hydrogen loss from each of the heterocycles are given as Supporting Information. Trends similar to those observed for homolytic hydrogen loss are again found, although changes in bond lengths are typically smaller.

Entropies (S°) and constant pressure heat capacities ($C_p(T)$ for $T = 300{-}1500$ K) have been calculated for each of the parent heterocycles and their anions and radicals, using the SMCPS program[26] with B3LYP/6-31G(d) vibrational frequencies and moments of inertia. The SMCPS program calculates entropies and heat capacities from statistical mechanical principles, according to the rigid-rotor-harmonic-oscillator approximation. SMCPS includes contributions from vibrational, translational, and external rotational motion, and also allows for the inclusion of electronic degeneracy (spin), internal rotational motion (with neglect of torsion frequencies), optical isomers, structure effects, and mass, where appropriate. The entropy and heat capacity results are provided in Table 3, along with the symmetry point group and ground-state electronic configuration of each species.

Enthalpies and Free Energies of Formation. *Isodesmic Enthalpies of Formation*. The enthalpies of formation of pyrrole,

TABLE 2: Bond Relaxation (Å) upon Homolytic Hydrogen Loss from the Five-Membered Nitrogen-Containing Heterocycles at the QCISD/6-311G(d,p) Level of Theory[a]

pyrrole

	N1−H	C2/5−H	C3/4−H
N1−C2	0.03	0.01	−0.01
N1−C5	0.03	−0.01	0.00
C2−C3	−0.09	0.01	0.01
C3−C4	0.07	−0.01	0.01
C4−C5	−0.09	0.00	0.00

pyrazole

	N1−H	C3−H	C4−H	C5−H
N1−N2	0.07	−0.01	0.00	−0.01
N1−C5	−0.09	0.00	0.00	0.02
N2−C3	−0.09	0.03	0.00	0.00
C3−C4	0.01	0.00	0.01	0.00
C4−C5	0.01	0.00	0.01	0.01

imidazole

	N1−H	C2−H	C4−H	C5−H
N1−C2	−0.01	0.01	0.00	0.00
N1−C5	0.06	−0.01	−0.01	0.01
C2−N3	−0.06	0.03	−0.01	0.00
N3−C4	0.07	−0.02	0.04	−0.01
C4−C5	−0.11	0.00	0.00	0.01

1,2,3-triazole

	N1−H	C4−H	C5−H
N1−N2	−0.04	0.00	−0.01
N1−C5	0.05	0.00	0.01
N2−N3	−0.09	−0.01	0.00
N3−C4	0.06	0.03	0.00
C4−C5	−0.11	0.00	0.01

1,2,4-triazole

	N1−H	C3−H	C5−H
N1−N2	0.08	−0.02	−0.01
N1−C5	−0.07	0.00	0.01
N2−C3	−0.12	0.02	0.00
C3−N4	0.05	0.02	−0.01
N4−C5	−0.03	−0.01	0.03

1*H*-tetrazole

	N1−H	C5−H		N1−H	C5−H
N1−N2	−0.09	0.01	N3−N4	−0.11	0.03
N1−C5	0.04	0.00	N4−C5	0.07	−0.03
N2−N3	0.26	0.00			

2*H*-tetrazole

	N1−H	C4−H		N1−H	C4−H
N1−N2	−0.22	0.00	N3−C4	−0.02	0.02
N1−N5	−0.07	−0.01	C4−N5	−0.06	0.02
N2−N3	0.04	−0.01			

[a] Bond relaxation = parent bond length − radical bond length. Atom numbering corresponds to that of Table 1.

pyrazole, and imidazole have been investigated using isodesmic work reactions. The isodesmic reaction schemes for each of these species are shown in Table 4, along with CBS-APNO, G3, and G3B3 reaction enthalpies. The isodesmic work reactions of Table 4 conserve not only the number and types of bonds, but also the aromaticity, ring structure, and number of radical electrons, leading to additional error cancellation over the corresponding atomization reactions. Enthalpies of formation calculated using the isodesmic reaction enthalpies of Table 4 are listed in Table 5, where the values from the three isodesmic work reactions have been averaged. The reaction enthalpies are relatively small, averaging 26 kcal mol^{-1}, indicating reasonable cancellation of energies across the work reactions. Enthalpies of formation for the reference species in the isodesmic work reactions are provided in Table 6. The enthalpies of formation presented in Table 5 will be compared to values calculated using atomization reactions, as well as to experimental values.

Atomization Enthalpies and Free Energies of Formation. For each of the heterocycles, enthalpies and free energies of formation have been obtained from atomization calculations, using the CBS-APNO, G3, and G3B3 composite theoretical methods. Tables 7 and 8 list respective $\Delta_f H^\circ_{298}$ and $\Delta_f G^\circ_{298}$ values for each of the nitrogen-containing heterocycles, calculated with the three theoretical methods. Also included in Tables 7 and 8 are weighted average enthalpies. The enthalpies of formation listed in Table 7 are compared to literature experimental values, where available, and to the enthalpies of formation for pyrrole, pyrazole, and imidazole calculated using isodesmic work reactions. There is typically good agreement between the average calculated enthalpies and the experimental enthalpies. The noticeable exception is 1*H*-tetrazole, where the average computational value is 81.2 kcal mol^{-1} and the experimental values are 78.1 and 76.6 kcal mol^{-1}. To our knowledge, enthalpies of formation for 1,2,3-triazole and 2*H*-tetrazole, which we calculate to be 63.9 and 79.2 kcal mol^{-1}, respectively, have not been previously determined.

In Table 7 we find that the enthalpies of formation for pyrrole and pyrazole calculated from isodesmic work reactions are in good agreement with both the enthalpies from atomization reactions and the experimental enthalpies. The isodesmic and atomization enthalpies differ by less than 0.5 kcal mol^{-1}, which is within the computational error of the theoretical methods. However, there is a significant difference between the enthalpy values for imidazole calculated using isodesmic and atomization work reactions, while the isodesmic value also differs significantly from the three previous experimental enthalpies. The atomization and isodesmic values vary by 2.1 kcal mol^{-1}, which is greater than the error expected for these theoretical methods, suggesting that one of the reference enthalpies is in error. Pyrimidine is the only reference species unique to the imidazole work reactions, and it is therefore likely that the literature enthalpy of formation of 46.80 ± 0.36 kcal mol^{-1} for pyrimidine[38] is high by 1−3 kcal mol^{-1}. Using an atomization work reaction, we calculate the enthalpy of formation of pyrimidine to be 44.5, 45.4, and 44.9 kcal mol^{-1} with the CBS-APNO, G3, and G3B3 methods, respectively, providing further evidence that the pyrimidine enthalpy of formation is incorrect. Accordingly, we recommend a weighted average enthalpy of formation of 44.8 ± 1.0 kcal mol^{-1} for pyrimidine.

From Tables 7 and 8 we find that, in general, the enthalpies and free energies of formation increase uniformly with increasing number of nitrogen atoms, by around 19 kcal mol^{-1} per nitrogen atom. However, imidazole and 1,2,4-triazole are the exception to this observation, with their enthalpies being around 10−15 kcal mol^{-1} below those of their respective isomers pyrazole and 1,2,3-triazole. Imidazole and pyrazole differ in that there are a C−C bond and a N−N bond in pyrazole versus two C−N bonds in imidazole. The increased stability of imidazole over pyrazole is accounted for by the C−C bond being around 10 kcal mol^{-1} stronger than the C−N bond, and the N−N bond being around 40 kcal mol^{-1} weaker than the C−N bond. Similarly, 1,2,3-triazole and 1,2,4-triazole differ in that there are a N═N double bond and a C═C double bond in 1,2,3-triazole versus two C═N double bonds in 1,2,4-triazole, where the N═N bond is around 40 kcal mol^{-1} weaker than the C═C bond, while the C═C and C═N bonds are of similar strength.

TABLE 3: Symmetry Point Group, Electronic Configuration, Entropy ($S°$), and Heat Capacity ($C_p(T)$) for the Five-Membered Nitrogen-Containing Heterocycles and Their Anions and Radicals from B3LYP/6-31G(d) Calculations[a]

	point group	electronic configuration	$S°$	C_p(300 K)	C_p(400 K)	C_p(500 K)	C_p(600 K)	C_p(800 K)	C_p(1000 K)	C_p(1500 K)
pyrrole	C_{2v}	$^1A_1$	64.62	17.00	22.81	27.69	31.57	37.21	41.13	47.07
1-pyrrolyl	C_{2v}	$^2A_2$	65.60	16.36	21.72	26.13	29.59	34.53	37.89	42.85
2-pyrrolyl	C_s	^2A	68.22	17.07	22.02	26.20	29.54	34.35	37.65	42.60
3-pyrrolyl	C_s	^2A	67.33	16.63	21.72	25.97	29.35	34.22	37.56	42.56
1-pyrrolide	C_{2v}	$^1A_1$	63.83	15.90	21.28	25.77	29.32	34.42	37.90	42.95
2-pyrrolide	C_s	^1A	66.16	17.02	22.27	26.58	29.96	34.78	38.07	42.93
3-pyrrolide	C_1	^1A	67.57	17.44	22.54	26.76	30.10	34.90	38.18	43.03
pyrazole	C_s	^1A	65.19	15.44	20.66	25.11	28.66	33.76	37.24	42.40
1-pyrazolyl	C_{2v}	$^2A_2$	65.60	15.92	20.61	24.42	27.38	31.54	34.30	38.30
3-pyrazolyl	C_1	^2A	68.23	16.51	21.08	24.81	27.70	31.75	34.46	38.38
4-pyrazolyl	C_s	^2A	66.35	14.90	19.43	23.29	26.36	30.72	33.64	37.87
5-pyrazolyl	C_s	^2A	66.59	15.11	19.62	23.45	26.50	30.82	33.71	37.91
1-pyrazolide	C_{2v}	$^1A_1$	63.23	14.60	19.41	23.44	26.61	31.08	34.06	38.27
3-pyrazolide	C_1	^1A	66.98	16.52	21.09	24.81	27.70	31.75	34.46	38.38
4-pyrazolide	C_s	^1A	67.41	15.64	20.11	23.93	26.96	31.26	34.12	38.23
5-pyrazolide	C_s	^1A	64.98	14.98	19.71	23.67	26.76	31.12	34.01	38.14
imidazole	C_s	^1A	65.24	15.56	20.76	25.19	28.72	33.80	37.27	42.41
1-imidazolyl	C_{2v}	$^2B_1$	64.92	14.94	19.64	23.58	26.68	31.06	33.98	38.16
2-imidazolyl	C_s	^2A	66.70	15.38	19.85	23.61	26.60	30.86	33.73	37.91
4-imidazolyl	C_s	^2A	66.32	15.05	19.59	23.42	26.46	30.79	33.68	37.89
5-imidazolyl	C_s	^2A	66.56	15.14	19.65	23.46	26.50	30.82	33.71	37.90
1-imidazolide	C_{2v}	$^1A_1$	63.01	14.17	18.92	22.97	26.19	30.79	33.85	38.17
2-imidazolide	C_s	^1A	65.71	15.96	20.61	24.42	27.38	31.52	34.28	38.27
4-imidazolide	C_s	^1A	68.08	16.56	21.03	24.71	27.60	31.67	34.40	38.36
5-imidazolide	C_s	^1A	65.13	15.28	19.97	23.86	26.91	31.21	34.07	38.18
1,2,3-triazole	C_s	^1A	64.67	14.43	19.12	23.10	26.24	30.67	33.61	37.86
1,2,3-triazol-1-yl	C_1	^2A	66.51	15.08	19.18	22.47	24.99	28.44	30.67	33.76
1,2,3-triazol-4-yl	C_s	^2A	65.74	13.91	17.97	21.37	24.02	27.70	30.07	33.37
1,2,3-triazol-5-yl	C_s	^2A	65.86	13.98	18.02	21.41	24.06	27.72	30.08	33.37
1,2,3-triazol-1-ide	C_{2v}	$^1A_1$	62.67	13.37	17.58	21.14	23.91	27.76	30.23	33.59
1,2,3-triazol-4-ide	C_s	^1A	65.46	14.85	18.91	22.25	24.81	28.32	30.56	33.67
1,2,3-triazol-5-ide	C_s	^1A	64.34	13.77	17.95	21.43	24.14	27.86	30.23	33.50
1,2,4-triazole	C_s	^1A	64.55	14.08	18.65	22.62	25.80	30.35	33.38	37.75
1,2,4-triazol-1-yl	C_{2v}	$^2A_2$	64.70	14.35	18.44	21.81	24.43	28.05	30.39	33.63
1,2,4-triazol-3-yl	C_s	^2A	65.72	13.73	17.68	21.05	23.73	27.48	29.91	33.29
1,2,4-triazol-5-yl	C_s	^2A	65.86	13.98	18.02	21.41	24.06	27.72	30.08	33.37
1,2,4-triazol-1-ide	C_{2v}	$^1A_1$	62.47	12.93	17.06	20.63	23.47	27.44	30.00	33.49
1,2,4-triazol-3-ide	C_1	^1A	67.49	15.42	19.32	22.51	24.98	28.40	30.61	33.69
1,2,4-triazol-5-ide	C_s	^1A	64.53	13.90	17.99	21.43	24.12	27.82	30.19	33.48
1*H*-tetrazole	C_s	^1A	64.25	13.45	17.52	20.99	23.72	27.49	29.92	33.29
1*H*-tetrazol-1-yl	C_{2v}	$^2B_1$	65.54	14.84	18.09	20.67	22.65	25.33	26.99	29.19
1*H*-tetrazol-2-yl	C_s	^2A	65.57	13.30	16.72	19.54	21.72	24.66	26.46	28.84
1*H*-tetrazol-1-ide	C_{2v}	$^1A_1$	62.12	12.09	15.66	18.73	21.12	24.37	26.36	28.91
1*H*-tetrazol-2-ide	C_s	^1A	64.16	13.17	16.74	19.66	21.88	24.83	26.62	28.94
2*H*-tetrazole	C_s	^1A	64.06	13.07	17.10	20.60	23.38	27.26	29.75	33.21
2*H*-tetrazol-1-yl	C_{2v}	$^2B_1$	65.54	14.84	18.09	20.67	22.65	25.33	26.99	29.19
2*H*-tetrazol-3-yl	C_s	^2A	65.20	12.68	16.11	19.03	21.31	24.40	26.30	28.77
2*H*-tetrazol-1-ide	C_{2v}	$^1A_1$	62.12	12.09	15.66	18.73	21.12	24.37	26.36	28.91
2*H*-tetrazol-3-ide	C_s	^1A	64.95	13.73	17.18	20.01	22.17	25.03	26.76	29.02

[a] Entropy and heat capacity values in cal mol^{-1} K^{-1}. Entropy corrections of $-R \ln \sigma$ added for molecular symmetry and $+R \ln 2$ added for unpaired electrons in radicals.

Accordingly, 1,2,4-triazole is considerably more stable than 1,2,3-triazole.

Figure 1 shows a plot of the calculated enthalpies of formation versus the number of nitrogen atoms in the molecule for each of the heterocycles. For pyrrole and pyrazole we have used the enthalpies calculated from isodesmic work reactions, while for the remaining molecules we have used enthalpies from atomization calculations. A good linear relationship is observed in Figure 1 among the enthalpies for pyrrole, pyrazole, 1,2,3-triazole, 1*H*-tetrazole, and 2*H*-tetrazole. This linear relationship predicts the enthalpies of formation of the five heterocycles to within an average error of 1.2 kcal mol^{-1} and a maximum error of 1.6 kcal mol^{-1}, versus our calculated enthalpies. If the relationship presented in Figure 1 is extrapolated to five nitrogen atoms, it predicts the enthalpy of formation of pentazole as being 98.4 kcal mol^{-1}. A similar figure showing the relationship between free energy of formation and the number of nitrogen atoms is provided in the Supporting Information, and this relationship predicts a free energy of formation of 79.4 kcal mol^{-1} for pentazole. Comparatively, CBS-APNO atomization calculations on pentazole provide an enthalpy of formation of 108.9 kcal mol^{-1} and a free energy of formation of 89.9 kcal mol^{-1}, in relatively good agreement with our predicted values. The high enthalpy of pentazole means that it will decompose to $N_2 + N_3H$ in a highly exothermic process, and it is unlikely that pentazole would exist as a stable species.

Bond Dissociation Energies. Bond dissociation energies corresponding to homolytic hydrogen loss from each of the carbon and nitrogen sites in the nitrogen-containing heterocycles have been calculated using the CBS-APNO, G3, and G3B3 theoretical methods, with both nonisodesmic and isodesmic work reactions. BDEs calculated with the three theoretical methods

TABLE 4: Isodesmic Work Reactions for Pyrrole, Pyrazole, and Imidazole and Reaction Enthalpies Calculated with the G3, G3B3, and CBS-APNO Theoretical Methods

	$\Delta_{rxn}H°_{298}$ (kcal mol^{-1})		
	G3	G3B3	CBS-APNO
pyrrole			
pyrrole + benzene + $NH_2^\bullet$ + CH_4 → pyridine + cyclopentadiene + NH_3 + $CH_3^\bullet$	16.64	16.68	18.45
pyrrole + benzene + $NH_2^\bullet$ + $CH_2{=}CH_2$ → pyridine + cyclopentadiene + NH_3 + $CH_2{=}CH^\bullet$	22.71	22.49	24.18
pyrrole + benzene + $NH_2^\bullet$ + CH_3CH_3 → pyridine + cyclopentadiene + NH_3 + $CH_3CH_2^\bullet$	13.57	13.39	14.85
pyrazole			
pyrazole + benzene + $NH_2^\bullet$ + CH_4 → pyridazine + cyclopentadiene + NH_3 + $CH_3^\bullet$	33.94	33.91	35.38
pyrazole + benzene + $NH_2^\bullet$ + $CH_2{=}CH_2$ → pyridazine + cyclopentadiene + NH_3 + $CH_2{=}CH^\bullet$	40.01	39.72	41.10
pyrazole + benzene + $NH_2^\bullet$ + CH_3CH_3 → pyridazine + cyclopentadiene + NH_3 + $CH_3CH_2^\bullet$	30.87	30.62	31.77
imidazole			
imidazole + benzene + $NH_2^\bullet$ + CH_4 → pyrimidine + cyclopentadiene + NH_3 + $CH_3^\bullet$	22.35	22.44	24.45
imidazole + benzene + $NH_2^\bullet$ + $CH_2{=}CH_2$ → pyrimidine + cyclopentadiene + NH_3 + $CH_2{=}CH^\bullet$	28.41	28.25	30.18
imidazole + benzene + $NH_2^\bullet$ + CH_3CH_3 → pyrimidine + cyclopentadiene + NH_3 + $CH_3CH_2^\bullet$	39.72	40.01	41.10

TABLE 5: Standard Enthalpies of Formation ($\Delta_fH°_{298}$) of Pyrrole, Pyrazole, and Imidazole Calculated from Isodesmic Reaction Enthalpies

	$\Delta_fH°_{298}$ (kcal mol^{-1})			
	G3	G3B3	CBS-APNO	av[a]
pyrrole	27.22	27.34	25.70	26.49
pyrazole	42.95	43.14	41.80	42.42
imidazole	34.81	34.88	33.00	33.92

[a] Weighted average: 0.25, G3; 0.25, G3B3; 0.5, CBS-APNO.

TABLE 6: Experimental Enthalpies of Formation for Isodesmic Work Reaction Reference Species (kcal mol^{-1})

	$\Delta_fH°_{298}$
benzene	19.82 ± 0.12[27]
1,3-cyclopentadiene	33.2[28]
CH_4	−17.89 ± 0.08[29]
$CH_3^\bullet$	35.05 ± 0.07[30]
$CH_2{=}CH_2$	12.54 ± 0.07[31]
$CH_2{=}CH^\bullet$	70.9 ± 0.3[32]
CH_3CH_3	−20.04 ± 0.07[33]
$CH_3CH_2^\bullet$	29.0 ± 0.4[34]
NH_3	−10.97[31]
NH_2	44.5 ± 0.1[35]
pyridine	33.50[36]
pyridazine	66.53 ± 0.3[37]
pyrimidine[a]	46.80 ± 0.36[38]

[a] The pyrimidine enthalpy is corrected in this study to 44.8 kcal mol^{-1} (see the text).

are provided in Table 9, where we find that there is relatively little variation between the three different methods. The BDEs calculated using the isodesmic and nonisodesmic work reactions are also in good agreement.

Average BDEs calculated using the nonisodesmic and isodesmic work reactions are reported in Table 10 for the respective molecules; these are compared to experimental values where available. The calculated N−H BDEs in pyrrole, pyrazole, and imidazole typically agree with the experimental values. It should be noted that the four experimental values for the N−H BDE in pyrrole differ by over 10 kcal mol^{-1}, highlighting the inaccuracy in some of the experimental BDE measurements. Our calculation of the pyrrole N−H BDE agrees best with the measurement of Bordwell et al.[10] Our calculated C−H bonds in pyrrole are near 120.4 kcal mol^{-1} for both bonds, which is about 8 kcal mol^{-1} higher than the experimental values of Blank et al.[12]

The lowest N−H BDE calculated is for pyrrole, at 96.0 kcal mol^{-1}, and this bond is around 10 kcal mol^{-1} weaker than the N−H bond in NH_3 (107.6 kcal mol^{-1}). The N−H BDEs in the five-membered nitrogen-containing heterocycles increase, in general, with increasing number of nitrogen atoms. Further analysis reveals that this effect is due to the presence of a nitrogen atom adjacent to the NH group. In pyrrole and imidazole, where there are no neighboring N atoms, the respective N−H bond energies are 96.0 and 96.2 kcal mol^{-1}. For 2*H*-tetrazole, with two N atoms adjacent to the NH group, the N−H bond energy is 115.4 kcal mol^{-1}, while the remaining N−H BDEs (all with one adjacent N atom) are between 110.4 and 113.3 kcal mol^{-1}.

The effect of a neighboring N atom on N−H bond energies could be to either stabilize the parent molecule through a favorable interaction of the NH group with the lone pair electrons on the adjacent nitrogen atom or to destabilize the nitrogen-centered radical through the unfavorable dipole−dipole interaction of the radical electron with the lone pair electrons on the adjacent nitrogen atom. Later, we calculate electron affinities for the nitrogen-centered radical heterocycles, which also show a similar increase due to the presence of an adjacent nitrogen atom. As such, we can attribute the bond energy trends to an effect in the radical species and not the parent heterocycles.

TABLE 7: Standard Enthalpies of Formation ($\Delta_fH°_{298}$) of Pyrrole, Imidazole, Pyrazole, 1,2,3-Triazole, 1,2,4-Triazole, and Tetrazole from G3, G3B3, and CBS-APNO Calculations

	$\Delta_fH°_{298}$ (kcal mol^{-1})				
	G3	G3B3	CBS-APNO	av[a]	literature
pyrrole	27.4	27.0	24.9	26.1 (26.5[b])	25.88 ± 0.12[14]
pyrazole	44.1	43.4	41.9	42.8 (42.4[b])	42.9 ± 0.2,[15] 43.3 ± 2.1[16]
imidazole	33.0	32.3	31.2	31.9 (33.9[b,c])	33.29 ± 0.45,[15] 31.8 ± 0.1,[16] 30.6 ± 1.8,[17] 31.6[39]
1,2,3-triazole	65.1	63.9	62.8	63.7	
1,2,4-triazole	47.8	46.8	46.3	46.8	46.1 ± 0.2,[15] 46.3 ± 0.45,[18] 46.4[39]
1*H*-tetrazole	82.4	80.7	80.4	81.0	78.1,[19] 76.6 ± 0.7,[20] 80.2[39]
2*H*-tetrazole	80.4	78.8	78.3	79.0	

[a] Weighted average: 0.25, G3; 0.25, G3B3; 0.5, CBS-APNO. [b] From isodesmic calculations. [c] A value of 31.9 kcal mol^{-1} using a pyrimidine enthalpy of 44.8 kcal mol^{-1}.

TABLE 8: Standard Free Energies of Formation ($\Delta_fG°_{298}$) of Pyrrole, Imidazole, Pyrazole, 1,2,3-Triazole, 1,2,4-Triazole, and Tetrazole from G3, G3B3, and CBS-APNO Calculations

	$\Delta_fG°_{298}$ (kcal mol^{-1})			
	G3	G3B3	CBS-APNO	av[a]
pyrrole	5.4	4.9	3.0	4.1
imidazole	11.5	10.7	9.7	10.4
pyrazole	22.6	21.8	20.5	21.4
1,2,3-triazole	44.5	43.2	42.3	43.1
1,2,4-triazole	27.2	26.1	25.8	26.2
1*H*-tetrazole	62.5	60.8	60.7	61.2
2*H*-tetrazole	60.6	59.0	58.6	59.2

[a] Weighted average: 0.25, G3; 0.25, G3B3; 0.5, CBS-APNO.

TABLE 9: BDEs for N−H and C−H Bonds in the Five-Membered Nitrogen-Containing Heterocycles from Nonisodesmic and Isodesmic Work Reactions with the G3, G3B3, and CBS-APNO Theoretical Methods

	nonisodesmic work reactions			isodesmic work reactions		
	G3	G3B3	CBS-APNO	G3	G3B3	CBS-APNO
			pyrrole			
N1−H	95.0	95.2	96.3	95.8	96.1	96.0
C2/5−H	120.7	119.7	120.8	120.8	120.1	120.2
C3/4−H	120.1	119.2	120.4	120.3	119.6	119.8
			pyrazole			
N1−H	111.3	109.2	112.4	112.1	110.1	112.1
C3−H	118.7	117.8	118.5	118.8	118.2	117.8
C4−H	122.2	121.0	121.9	122.4	121.3	121.2
C5−H	121.1	119.9	120.7	121.2	120.3	120.0
			imidazole			
N1−H	92.7	96.0	97.5	93.5	96.9	97.2
C2−H	117.6	117.1	117.4	117.8	117.5	116.7
C4−H	118.4	117.8	118.3	118.6	118.1	117.6
C5−H	121.2	120.5	121.3	121.4	120.9	120.6
			1,2,3-triazole			
N1−H		109.4	110.7		110.4	110.4
C4−H	123.2	121.5	121.6	123.3	121.8	121.0
C5−H	124.5	122.7	123.1	124.7	123.0	122.4
			1,2,4-triazole			
N1−H		109.5	110.8		110.4	110.6
C3−H	119.9	119.3	119.7	120.1	119.6	119.0
C5−H	119.3	118.7	119.0	119.5	119.1	118.3
			1*H*-tetrazole			
N1−H	113.7	112.5	113.0	114.5	113.4	112.7
C5−H	124.1	122.6	122.4	124.2	123.0	121.8
			2*H*-tetrazole			
N1−H	115.7	114.4	115.1	116.5	115.3	114.9
C4−H	125.5	123.5	123.8	125.6	123.9	123.1

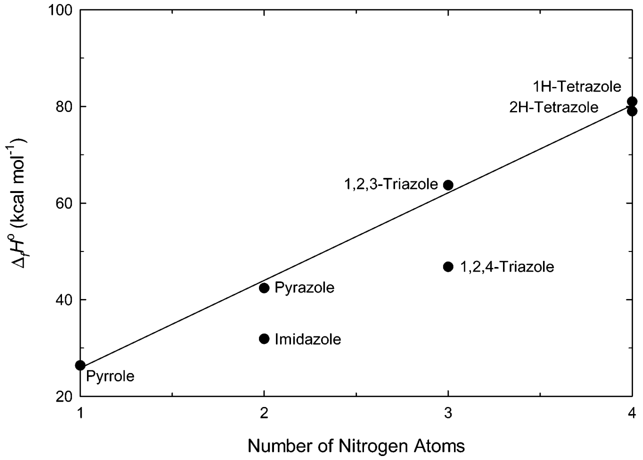


Figure 1. Enthalpies of formation of the five-membered nitrogen-containing heterocycles as a function of the number of nitrogen atoms in the molecule.

TABLE 10: Average BDEs for N−H and C−H Bonds in the Five-Membered Nitrogen-Containing Heterocycles and Comparison to Literature Values

	BDE (kcal mol^{-1})		
	nonisodesmic[a]	isodesmic[a]	literature
		pyrrole	
N1−H	95.7	96.0	96.6,[10] 99 ± 6,[11] 88 ± 2,[12] 92.6 ± 1[13]
C2/5−H	120.5	120.3	112.5 ± 1[12,b]
C3/4−H	120.0	119.9	112.5 ± 1[12,b]
		pyrazole	
N1−H	111.3	111.6	108.0 ± 0.4[9]
C3−H	118.4	118.2	
C4−H	121.8	121.5	
C5−H	120.6	120.4	121 ± 4[9]
		imidazole	
N1−H	95.9	96.2	96.5 ± 0.6[8]
C2−H	117.4	117.2	
C4−H	118.2	118.0	
C5−H	121.1	120.9	119 ± 4[8]
		1,2,3-triazole	
N1−H	110.1	110.4	
C4−H	122.0	121.8	
C5−H	123.4	123.1	
		1,2,4-triazole	
N1−H	110.2	110.5	
C3−H	119.7	119.4	
C5−H	119.0	118.8	
		1*H*-tetrazole	
N1−H	113.1	113.3	
C5−H	122.9	122.7	
		2*H*-tetrazole	
N1−H	115.1	115.4	
C4−H	124.2	123.9	

[a] Weighted average: 0.25, G3; 0.25, G3B3; 0.5, CBS-APNO. [b] C−H bond not specified.

The C−H BDEs in the seven nitrogen-containing heterocycles are all of similar value, and the effect of an adjacent NH group on these C−H BDEs seems negligible. The heterocycle C−H BDEs range from 118 to 125 kcal mol^{-1}, and therefore lie between the values of the $CH_2{=}CH{-}H$ (110.7 kcal mol^{-1}) and $CH{\equiv}C{-}H$ (133.3 kcal mol^{-1}) bonds.[40] These C−H bond energies are similar to those for other aromatic species, including the five-membered oxygen-containing heterocycle furan (cyclo-C_5OH_4), where C−H bond energies are on the order of 121−122 kcal mol^{-1},[41] and to a lesser extent benzene, where the C−H bond energy is 112.9 kcal mol^{-1}.[40]

N−H and C−H Acidity. Deprotonation enthalpies and free energies, $\Delta_{acid}H°_{298}$ and $\Delta_{acid}G°_{298}$, have been calculated for each hydrogen atom in the five-membered nitrogen-containing heterocycles using the CBS-APNO, G3, and G3B3 theoretical methods; the results are reported in Table 11, and are compared to available literature values. For pyrrole and imidazole we find excellent agreement between the calculated and experimental N−H $\Delta_{acid}G°_{298}$ values, with the largest error being only 0.2 kcal mol^{-1}. For pyrazole, the average error is 1.1 kcal mol^{-1}, which is significantly larger than that for pyrrole and imidazole, although it is still within the computational error. The N−H protons become more acidic with increasing number of nitrogen atoms, in opposition to the trend observed with the N−H BDEs. One possible explanation for this is increasing electronegativity of the NH group with increasing number of nitrogen atoms.

Each of the C−H protons in the five-membered nitrogen-containing heterocycles are less acidic than the N−H protons

TABLE 11: Deprotonation Enthalpies ($\Delta_{\mathrm{acid}}H^\circ_{298}$) and Free Energies ($\Delta_{\mathrm{acid}}G^\circ_{298}$) for N−H and C−H Bonds in the Five-Membered Nitrogen-Containing Heterocycles Calculated with the G3, G3B3, and CBS-APNO Theoretical Methods

	$\Delta_{\mathrm{acid}}H^\circ_{298}$ (kcal mol^{-1})					$\Delta_{\mathrm{acid}}G^\circ_{298}$ (kcal mol^{-1})				
	G3	G3B3	CBS-APNO	av[a]	literature	G3	G3B3	CBS-APNO	av[a]	literature
pyrrole										
N1−H	359.4	359.3	359.1	359.2	359.2 ± 0.4[7]	352.0	351.8	351.6	351.8	351.9 ± 0.4[7]
C2/5−H	396.5	396.1	396.0	396.2		388.3	387.9	387.9		
C3/4−H	407.1	406.5	407.4	407.1		398.8	397.9	399.0		
pyrazole										
N1−H	354.8	354.7	354.6	354.7	353.6 ± 0.4[9]	347.6	347.5	347.4	347.5	346.4 ± 0.3[9]
C3−H	401.0	400.5	401.7	401.2		393.0	392.2	393.4	393.0	
C4−H	397.5	397.2	397.3	397.3		389.4	388.8	389.0	389.1	
C5−H	384.9	384.6	384.8	384.8		377.2	376.9	377.1	377.1	380 ± 4[9]
imidazole										
N1−H	349.9	349.9	349.6	349.8	349.7 ± 0.5[8]	342.8	342.8	342.6	342.7	342.6 ± 0.4[8]
C2−H	390.2	389.9	389.8	389.9		382.3	382.0	382.0	382.1	
C4−H	404.4	404.6	405.4	405.0		396.8	396.0	397.0	396.7	
C5−H	388.4	388.2	388.1	388.2		380.7	380.4	380.4	380.5	380 ± 4[8]
1,2,3-triazole										
N1−H	342.1	342.1	341.9	342.0		334.9	334.9	334.7	334.8	
C4−H	393.0	392.7	392.8	392.8		385.0	384.7	384.9	384.9	
C5−H	374.7	374.4	374.5	374.5		367.0	366.8	366.8	366.9	
1,2,4-triazole										
N1−H	344.1	344.1	344.0	344.1		337.0	337.0	336.9	337.0	
C3−H	394.8	394.4	394.9	394.8		386.4	385.7	386.3	386.2	
C5−H	378.1	377.9	378.1	378.1		370.3	370.2	370.4	370.3	
1*H*-tetrazole										
N1−H	329.7	329.8	329.7	329.7		322.6	322.7	322.6	322.6	
C5−H	365.8	365.5	365.5	365.6		358.1	357.8	357.8	357.9	
2*H*-tetrazole										
N1−H	331.7	331.7	331.8	331.8		324.5	324.5	324.7	324.6	
C4−H	382.7	382.1	382.4	382.4		374.6	374.1	374.4	374.4	

[a] Weighted average: 0.25, G3; 0.25, G3B3; 0.5, CBS-APNO.

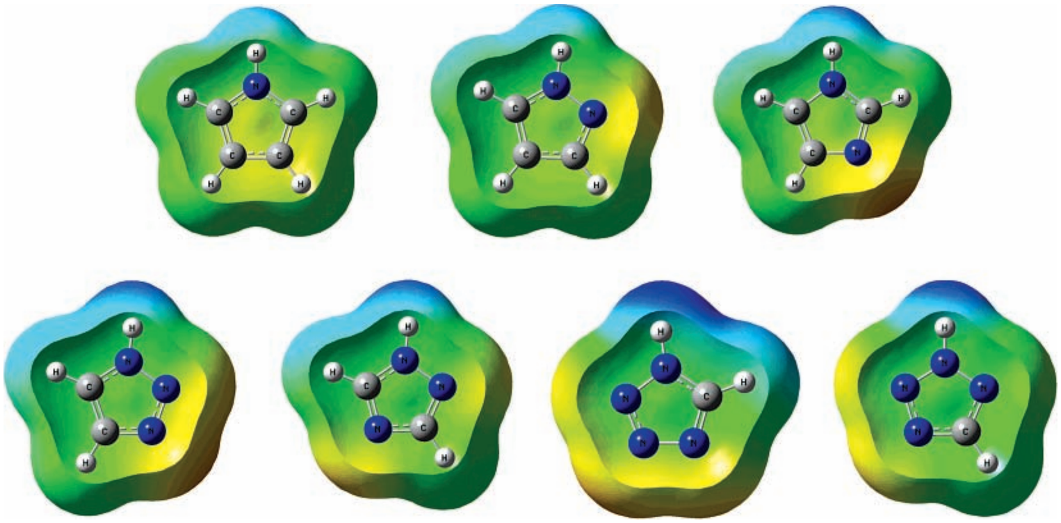


Figure 2. Electrostatic potential mapped onto the total electron density for the five-membered nitrogen-containing heterocycles. Charge ranges from −0.08327 (red) to +0.08327 (blue), with green neutral. Calculations are at the B3LYP/6-31G(d) level.

by between ca. 30 and 50 kcal mol^{-1}. Gianola et al.[8,9] noted that the presence of more acidic N−H protons in pyrazole and imidazole makes the C−H proton acidities difficult to measure. However, they were able to estimate the C5−H acidities in imidazole and pyrazole to be between the acidities of H_2O and the OH radical, giving a value of $\Delta_{\mathrm{acid}}G^\circ_{298} = 380 \pm 4$ kcal mol^{-1} for both imidazole and pyrazole. This result is supported by our calculations, which provide average C−H deprotonation free energies of 377.1 and 380.5 kcal mol^{-1} for pyrazole and imidazole, respectively. Gianola et al.[8,9] also proposed that the acidity of C−H protons is increased by the presence of an adjacent NH group. This finding is also reflected in our results, where a C−H proton adjacent to an NH group is, on average, 35 kcal mol^{-1} less acidic than that molecule's N−H proton, while the nonadjacent C−H protons are 49 kcal mol^{-1} less acidic, on average.

As discussed above, the electron-withdrawing effect of the NH group may be able to explain trends observed in N−H and C−H acidities. In Figure 2, the electrostatic potential for each of the heterocycles has been mapped onto the electron density surface, from B3LYP/6-31G(d) calculations. Immediately we notice that the positive charge on the NH group increases with increasing number of nitrogen atoms in the molecule, explaining why the N−H acidities also increase with the number of nitrogen

TABLE 12: Electron Affinities for the Radicals of the Five-Membered Nitrogen-Containing Heterocycles

	electron affinity (eV)	
	calcd[a]	exptl
1-pyrrolyl	2.18	2.145[7]
2-pyrrolyl	1.66	
3-pyrrolyl	1.18	
1-pyrazolyl	3.06	2.938[8]
3-pyrazolyl	1.36	
4-pyrazolyl	1.68	
5-pyrazolyl	2.16	2.104[8]
1-imidazolyl	2.64	2.613[9]
2-imidazolyl	1.80	
4-imidazolyl	1.19	
5-imidazolyl	2.04	1.992[9]
1,2,3-triazol-1-yl	3.55	
1,2,3-triazol-4-yl	1.88	
1,2,3-triazol-5-yl	2.72	
1,2,4-triazol-1-yl	3.47	
1,2,4-triazol-3-yl	1.70	
1,2,4-triazol-5-yl	2.38	
1-tetrazolyl	4.21	
2-tetrazolyl	3.09	
3-tetrazolyl	2.43	

[a] Weighted average: 0.25, G3; 0.25, G3B3; 0.5, CBS-APNO.

atoms. Furthermore, for all molecules with two or more CH groups we find that the CH group adjacent to the NH group is always more electropositive than the other CH group(s), explaining why CH protons are more acidic when adjacent to an NH group.

To further explore the effect of increasing nitrogen content on electron binding in these heterocycles, we have calculated electron affinities (EAs) for each of the heterocyclic radicals (Table 12). Our calculations are for 0 K energies, and are again the weighted average of G3, G3B3, and CBS-APNO results. Where available, our calculated EA values are compared to experimental measurements, and we find excellent agreement. For the nitrogen-centered radicals, the calculated EAs demonstrate a uniform increase as the nitrogen content of the heterocycle increases, indicating that the radical electron is becoming more weakly bound. Not surprisingly, this correlates with increasing electronegativity of the NH group in the parent heterocycles as the nitrogen content increases, and helps explain the observed trends in N−H acidities. Specifically, we can conclude that the lower N−H bond energies in pyrrole and imidazole, relative to the other heterocycles, are due to the absence of a destabilizing $N^{\bullet}$---N interaction with a neighboring N atom, as is present in the other heterocycles. In Table 12 we also see that electron affinities are greater for the carbon-centered radicals with an adjacent NH group by, on average, 0.67 eV (15 kcal mol^{-1}), which is in close agreement with the ca. 14 kcal mol^{-1} increase in acidity witnessed for C−H bonds adjacent to the NH group.

Conclusion

We have used ab initio and density functional theory methods to study the structure and thermochemistry of five-membered nitrogen-containing heterocycles. As well as calculating many new thermochemical properties, including enthalpies of formation, bond energies, and proton acidities, we have identified important trends in the behavior of these compounds and their anions and radicals. Our major findings are summarized below.

(1) Enthalpies of formation of pyrrole, pyrazole, imidazole, 1,2,3-triazole, 1,2,4-triazole, 1*H*-tetrazole, and 2*H*-tetrazole were calculated as 26.1, 42.8, 31.9, 63.7, 46.8, 81.0, and 79.0 kcal mol^{-1} via atomization work reactions, while the enthalpies of formation of pyrrole and pyrazole were also evaluated to be 26.5 and 42.4 kcal mol^{-1} using isodesmic work reactions, which help reduce computational errors. The six-membered heterocycle pyrimidine was used as a reference species in our isodesmic calculations, and its enthalpy was found to be in error. We calculate an enthalpy for this molecule of 44.8 ± 1.0 kcal mol^{-1}.

(2) A relationship is developed between the number of nitrogen atoms in a heterocycle and the heterocycle's enthalpy, and this relationship is extrapolated to predict an enthalpy of formation of 98.4 kcal mol^{-1} for the theorized molecule pentazole. Calculations at the CBS-APNO level of theory find this same value to be 108.9 kcal mol^{-1}.

(3) Bond dissociation energies and acidities for N−H and C−H hydrogen loss are calculated. C−H BDEs are found to be around 120 kcal mol^{-1} in all of the heterocycles, and in all cases the C−H BDEs are larger than the N−H BDEs. The N−H BDEs also increase when the NH group is adjacent to a nitrogen atom. Deprotonation enthalpies and free energies reveal that C−H protons are less acidic than N−H protons by ca. 49 kcal mol^{-1}, or ca. 35 kcal mol^{-1} when adjacent to the NH group. N−H protons are also found to become more acidic with increasing number of nitrogen atoms in the ring, and this is explained by increasing electronegativity of the NH group, as illustrated by electrostatic potential diagrams. Electron affinities are also calculated for all anions, and the results support our hypothesis explaining the effect of adjacent N atoms on N−H bond energies, where there is an unfavorable dipole−dipole interaction in the nitrogen-centered radical species.

Supporting Information Available: Molecular enthalpies and free energies (hartrees) for each of the heterocycles and their radicals and ions, QCISD/6-311G(d,p) bond lengths in the radicals and ions formed by H loss from each of the heterocycles and bond relaxation relative to the parent molecules, and a plot of the heterocycle free energy of formation versus the number of nitrogen atoms in the molecule. This material is available free of charge via the Internet at http://pubs.acs.org.

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