make predictions of the most stable form of MH_7P_2 species with bulkier phosphine ligands in solution more difficult, these results indicate a greater tendency for Tc to display nonclassical structures relative to Re. The positive ions of ReH_7L_2 and $Re(H_2)H_5L_2$ are also investigated, with the IP of the latter form calculated to be 2.1 eV lower in energy.

Ethynamine: The Remarkable Acid-Strengthening and Base-Weakening Effect of the Acetylenic Linkage. A Comparison with Ethenamine and Methylamine

Brian J. Smith and Leo Radom*

Contribution from the Research School of Chemistry, Australian National University, Canberra, A.C.T. 2601, Australia. Received April 15, 1991

Abstract: Ab initio molecular orbital calculations predict that ethynamine is a substantially stronger acid but a substantially weaker base than other amines such as methylamine and ethenamine in the gas phase, as previously observed experimentally for other ynamine systems in aqueous solution. The high relative acidity of ethynamine can be attributed largely to stabilization of the ethynylamide anion and the low relative basicity to a destabilization of the ethynylammonium cation. The preferred site of protonation in both ethynamine and ethenamine is at carbon rather than nitrogen, a result which can be rationalized in terms of stabilizing interactions in the C-protonated species. High-level (G2) theoretical data are presented for the related oxygen-containing systems, ethynol, vinyl alcohol, ketene, and acetaldehyde, and used to derive new values of the heats of formation for these molecules.

Introduction

In a recent experimental study of ynamines ($RC\equiv CNH_2$) in aqueous solution, Kresge and co-workers[1] reported basicities and acidities which differ dramatically from those of standard saturated amines. For example, phenyl(cyclohexylamino)acetylene ($PhC\equiv CNHC_6H_{11}$) was found to be more than 10 orders of magnitude less basic than cyclohexylamine, while phenylaminoacetylene ($PhC\equiv CNH_2$) was found to be more than 17 orders of magnitude more acidic than ammonia. The $C\equiv C$ triple bond clearly has a massive effect, and an understanding of the operative mechanism is highly desirable.

In previous related experiments, it had been found that ynols were considerably more acidic than enols.[2] For example, phenylynol ($PhC\equiv COH$) was found to be more acidic than $PhCH\equiv CHOH$ by more than 7 pK_a units. We subsequently examined the acidity of ynols using ab initio molecular orbital theory to see whether the very high acidity carried over to the gas phase.[3] Indeed, deprotonation of the prototype ynol, ethynol ($HC\equiv COH$), was calculated to require 101 kJ mol^{-1} less energy than deprotonation of its enol analogue, vinyl alcohol ($CH_2\equiv C$-HOH). By careful analysis of bond separation energies (BSEs), we were able to show that this greater acidity could be attributed to two contributing factors: (1) destabilization of the neutral ynol relative to the enol and (2) stabilization of the ynolate anion relative to the enolate anion.

It is the purpose of the present study to carry out a similar investigation of the acidities and basicities of ethynamine, the prototype ynamine. Ethynamine has attracted theoretical attention as a possible interstellar species.[4] It was observed for the first time by Schwarz, Holmes, and co-workers in neutralization-reionization mass spectrometry experiments,[5] and subsequently

Table I. Calculated Total Energies (hartrees) and Zero-Point Vibrational Energies (kJ mol^{-1})[a]

no.	species		HF/6-31+G*	MP4/6-311+G**	ZPVE[b]
1	$CH_3CHNH_2^+$	C_s	−133.443 82	−133.991 82	232.2
2	$CH_2\equiv CHNH_3^+$	C_s	−133.414 18	−133.969 92	236.4
3	$CH_3CH\equiv NH$	C_s	−133.077 08	−133.632 97	193.7
4	$CH_2\equiv CHNH_2$	C_1	−133.068 84	−133.626 39	194.4
5	$CH_2\equiv CHNH^-$	C_s	−132.449 51	−133.013 38	152.2
6	$CH_2\equiv CNH_2^+$	C_{2v}	−132.212 28	−132.727 02	161.7
7	$HC\equiv CNH_3^+$	C_{3v}	−132.169 13	−132.693 50	169.2
8	$CH_2\equiv C\equiv NH$	C_s	−131.876 54	−132.399 42	123.6
9	$HC\equiv CNH_2$	C_s	−131.852 87	−132.375 84	126.5
10	$HC\equiv CNH^-$	C_1	−131.252 63	−131.785 71	84.3
11	$HC\equiv CNH^-$	C_s	−131.249 52	−131.779 49	81.9[c]
12	$CH_3NH_3^+$	C_{3v}	−95.574 16	−95.989 63	223.5
13	CH_3NH_2	C_s	−95.214 17	−95.630 86	180.7
14	CH_3NH^-	C_s	−94.543 26	−94.969 40	133.0
15	CH_3CH_3	D_{3d}	−79.229 45	−79.614 80	208.8
16	$CH_3CH_2^+$	C_{2v}	−78.310 18	−78.653 25	170.7
17	$CH_2\equiv CH_2$	D_{2h}	−78.035 82	−78.383 34	143.6
18	$CH_2\equiv CH^+$	C_{2v}	−77.076 07	−77.392 25	96.1
19	$HC\equiv CH$	$D_{\infty h}$	−76.823 07	−77.140 00	77.2
20	$CH_2\equiv NH$	C_s	−94.032 67	−94.412 05	113.4
21	$CH_2\equiv O$	C_{2v}	−113.871 16	−114.267 28	76.5
22	CH_4	T_d	−40.195 67	−40.405 13	125.1
23	H_2	$D_{\infty h}$	−1.126 83	−1.167 64	27.8

[a] HF/6-31+G* optimized structures. [b] Zero-point vibrational energies (HF/6-31+G*). [c] Structure has one imaginary frequency.

some of its infrared absorptions have been recorded by Wentrup et al.[6] The focus in this paper will be on the acid–base properties of ethynamine. Comparisons will be presented with ethenamine, the prototype enamine, and with methylamine. A particular point of interest is to understand why the preferred site of protonation

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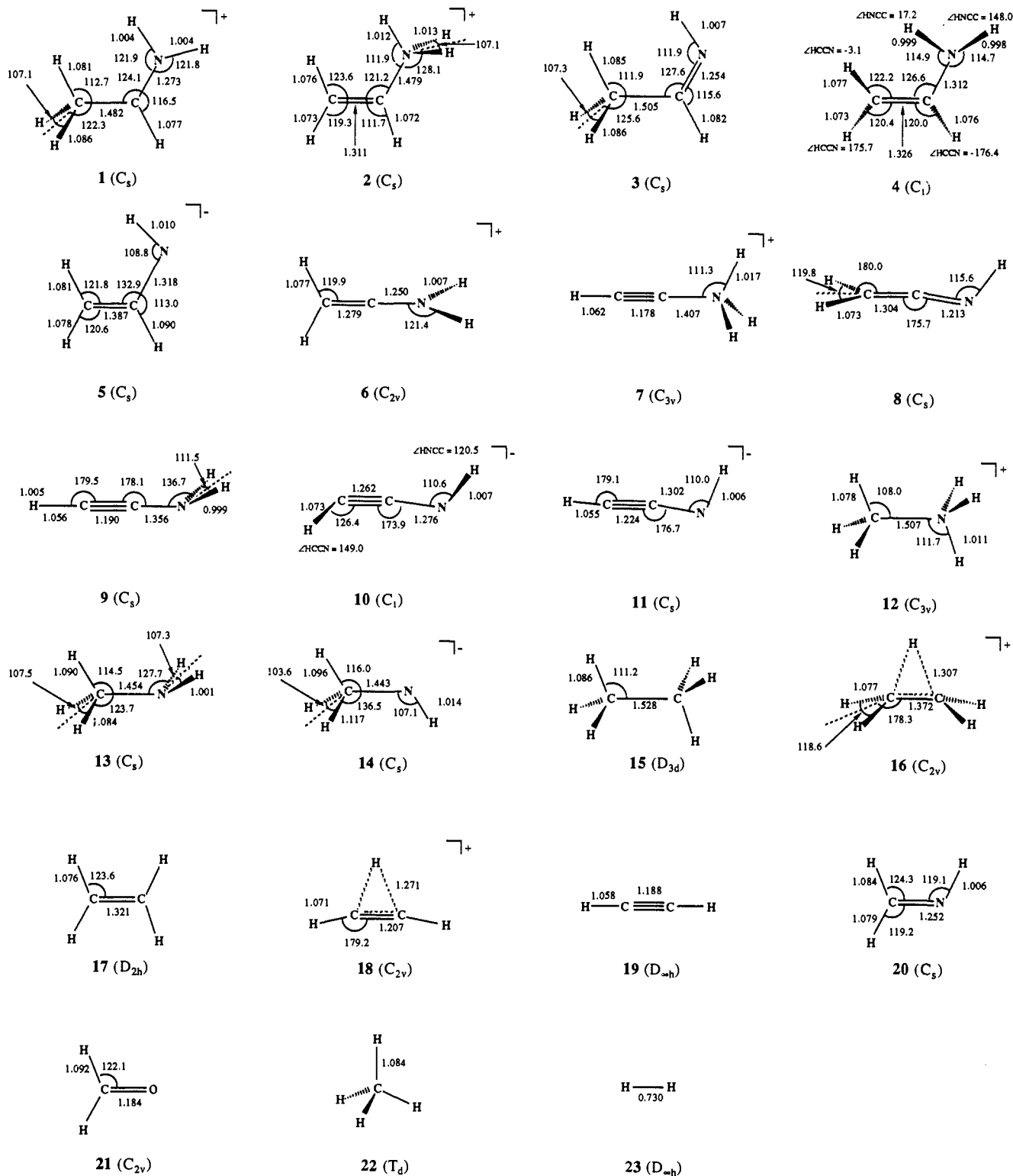
Figure 1. Optimized structures at the HF/6-31+G* level. Bond lengths in angstroms and bond angles in degrees.

of ethynamine is on carbon rather than on nitrogen.

Method

Standard ab initio molecular orbital calculations[7] were carried out with the GAUSSIAN 88[8] and GAUSSIAN 90[9] systems of programs. Optimized

geometries and zero-point vibrational energies were obtained at the HF/6-31+G* level. Improved energies were obtained by performing MP4/6-311+G** calculations at the HF/6-31+G* optimized geometries. Listed in Table I are the calculated total energies at both the HF/6-31+G* and MP4/6-311+G** levels, along with the calculated zero-point vibrational energies. Reaction energies of interest are presented and compared with available experimental data[10] in Table II.

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Table II. Calculated and Experimental Reaction Energies (kJ mol⁻¹)[a]

reaction	energy		
	ΔE[b]	ΔE[c]	ΔE_{expt}[d]
(1) CH_2=C=NH → HC≡CNH$_2$	62	65	
(2) CH_3CH=NH → CH_2=CHNH$_2$	17	18	21
(3) HC≡CNH$_2$ → HC≡CNH⁻ + H⁺	1549	1511	
(4) CH_2=C=NH → HC=C=NH⁻ + H⁺	1611	1576	
(5) CH_2=CHNH$_2$ → CH_2=CHNH⁻ + H⁺	1609	1572	
(6) CH_3CH=NH → CH_2=CHNH⁻ + H⁺	1627	1589	
(7) HC≡CNH$_2$ + CH$_4$ → HC≡CH + CH$_3$NH$_2$	27	32	
(8) CH_2=CHNH$_2$ + CH$_4$ → CH_2=CH$_2$ + CH$_3$NH$_2$	45	50	76
(9) HC≡CNH⁻ + CH$_4$ → HC≡CH + CH$_3$NH⁻	214	215	
(10) CH_2=CHNH⁻ + CH$_4$ → CH_2=CH$_2$ + CH$_3$NH⁻	173	172	
(11) HC≡CNH$_2$ + H⁺ → HC≡CNH$_3$⁺	-834	-795	
(12) HC≡CNH$_2$ + H⁺ → CH_2=CNH$_2$⁺	-922	-890	
(13) CH_2=CHNH$_2$ + H⁺ → CH_2=CHNH$_3$⁺	-902	-864	
(14) CH_2=CHNH$_2$ + H⁺ → CH$_3$CHNH$_2$⁺	-959	-925	-896
(15) HC≡CNH$_3$⁺ + CH$_4$ → HC≡CH + CH$_3$NH$_3$⁺	-81	-76	
(16) CH_2=CHNH$_3$⁺ + CH$_4$ → CH_2=CH$_2$ + CH$_3$NH$_3$⁺	5	11	
(17) CH$_3$NH$_2$ → CH$_3$NH⁻ + H⁺	1737	1694	1681
(18) CH$_3$NH$_2$ + H⁺ → CH$_3$NH$_3$⁺	-942	-903	-890
(19) HC≡CH + H⁺ → CH_2=CH⁺	-662	-645	-636
(20) CH_2=CNH$_2$⁺ → HC≡CNH$_3$⁺	88	95	
(21) CH_2=CNH$_2$⁺ + CH$_4$ → CH_2=CH⁺ + CH$_3$NH$_2$	286	277	
(22) CH_2=CH$_2$ + H⁺ → CH$_3$CH$_2$⁺	-709	-684	-674
(23) CH$_3$CHNH$_2$⁺ → CH_2=CHNH$_3$⁺	58	61	
(24) CH$_3$CHNH$_2$⁺ + CH$_4$ → CH$_3$CH$_2$⁺ + CH$_3$NH$_2$	296	291	297

[a] Calculated using total energies from Table I. [b] MP4/6-311+G** values. [c] MP4/6-311+G** values together with zero-point vibrational corrections (scaled by 0.9). [d] Experimental values at 0 K evaluated using data from ref 10 and, where necessary, theoretical temperature corrections.

Optimized geometries (**1–23**) are displayed in Figure 1. Throughout this paper, the terms acidity and basicity refer, respectively, to *enthalpies* (rather than *free energies*) of deprotonation (ΔH_{acid}) and protonation (proton affinity, denoted PA) reactions.

Discussion

Structural Considerations. Most of the structures calculated in this study are reasonably straightforward and do not warrant further comment. For the ethynylamide anion (HC≡CNH⁻), however, previous calculations[11] at the HF/4-31G level predicted a planar arrangement. Our calculations at a higher level of theory indicate that the planar C_s structure (**11**) has one imaginary frequency and distorts to a C_1 structure (**10**) when the symmetry constraint is removed. Inspection of the Mulliken total atomic charges shows approximately equal charges of -0.63 e and -0.61 e on the N and C(H) atoms, respectively, for the C_1 isomer (**10**), suggesting significant contributions from both imine (**24**) and acetylenic (**25**) valence structures. In contrast, charges for the C_s isomer (**11**) of -1.05 e and -0.17 e for the N and C(H) atoms, respectively, indicate a domination by the acetylenic valence structure (**25**). These differences are reflected in the calculated structural parameters for **10** and **11** (Figure 1).

$$\underset{\mathbf{24}}{\overline{HC}=\underline{C}=NH} \qquad \underset{\mathbf{25}}{HC≡\underline{C}—\overline{N}H}$$

Calculated and Experimental Thermochemical Information. In our previous communication regarding the remarkably high acidity of ethynol,[3] we were able to show that the level of calculation used was capable of reproducing available experimental estimates of reaction energies with good accuracy. Here again we find a satisfactory level of agreement in the few cases where comparisons are possible (Table II) except for two reactions, (8) and (14),

Table III. Calculated Heats of Formation (kJ mol⁻¹)[a]

molecule	$\Delta H_f°_0$			$\Delta H_f°_{298}$		
	G2	MP4/6-311+G**	exptl[b]	G2	MP4/6-311+G**	exptl[b]
CH$_3$CH=O	-153	-151	-155	-164	-162	-166
CH_2=CHOH	-113	-113	-115[c]	-124	-124	-125
CH_2=C=O	-43	-50	-45	-47	-53	-48
HC≡COH	95	96		92	93	
CH$_3$CH=NH (3)		52			41	8
CH_2=CHNH$_2$ (4)		70			55	29
CH_2=C=NH (8)		182			175	
HC≡CNH$_2$ (9)		255			249	

[a] Evaluated from bond separation energies together with experimental heats of formation for reference molecules (see refs 10, 16, and 17). [b] From ref 10, unless otherwise noted. [c] Calculated from the $\Delta H_f°_{298}$ value in ref 10 together with the theoretical temperature correction to 0 K.

involving CH_2=CHNH$_2$ (**4**) where the calculated and experimental reaction energies differ by 26 and 29 kJ mol⁻¹, respectively. However, we note that the tabulated value[10] for the "experimental" heat of formation for CH_2=CHNH$_2$ (**4**) (29 kJ mol⁻¹) is in fact derived from an approximate heat of formation[12] for CH$_3$CH=NH (**3**) (8 ± 17 kJ mol⁻¹) and a theoretical isomerization energy[13,14] between **3** and **4** (21 kJ mol⁻¹), and so the experimental energies for reactions 8 and 14 are associated with considerable uncertainty.

Our direct calculations indicate an energy difference at 0 K between ethynamine (HC≡CNH$_2$, **9**) and ketene imine (CH_2=C=NH, **8**) of 65 kJ mol⁻¹, significantly larger than the ethenamine (CH_2=CHNH$_2$, **4**) – acetaldimine (CH$_3$CH=NH, **3**) difference of 18 kJ mol⁻¹. A similar but even more pronounced trend was observed[3] for the ethynol–ketene (155 kJ mol⁻¹) and ethenol–acetaldehyde (56 kJ mol⁻¹) energy differences, calculated at the same level of theory as used here.

In light of the uncertainties in the experimental heats of formation of CH$_3$CH=NH (**3**) and CH_2=CHNH$_2$ (**4**), and the absence of experimental values for CH_2=C=NH (**8**) and HC≡CNH$_2$ (**9**), we have estimated new values. These were obtained from our calculated values of the appropriate bond separation energies[15] together with experimental heats of formation ($\Delta H_f°$)[10,16] of the other species involved in the corresponding bond separation reactions. Heats of formation for formaldimine (CH$_2$=NH) of 86 (94) kJ mol⁻¹ at 298 K (0 K), required for this analysis, were taken from our recent reevaluation.[17] Values obtained in this manner for $\Delta H_f°_{298}$ ($\Delta H_f°_0$) are summarized in Table III. These heats of formation lead to improved energy differences between **8** and **9** at 298 K of 74 kJ mol⁻¹ and between **3** and **4** of 14 kJ mol⁻¹.

In order to assess the likely accuracy of these results, we have carried out a parallel evaluation of heats of formation for CH$_3$CH=O, CH_2=CHOH, CH_2=C=O, and HC≡COH for which available experimental data and higher level theoretical data are more extensive. Results at the MP4/6-311+G** level are compared with experimental values and with theoretical values obtained using energies calculated at the somewhat higher G2 level of theory[18,19] in Table III. It can be seen that the G2, MP4/6-

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(16) Experimental heats of formation at 298 K (0 K), taken from ref 10 and used in the analysis, are (kJ mol⁻¹) -74.5 (-66.8) for CH$_4$, -84.0 (-68.4) for CH$_3$CH$_3$, 52.2 (60.7) for CH_2=CH$_2$, 228.0 (228.6) for HC≡CH, -23.0 for CH$_3$NH$_2$, -201.6 (-190.7) for CH$_3$OH, and -108.7 (-104.7) for CH_2=O. Values (kJ mol⁻¹) of 86 (94) for CH_2=NH and -8.0 at 0 K for CH$_3$NH$_2$ were taken from ref 17.

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Effect of the Acetylenic Linkage

J. Am. Chem. Soc., Vol. 114, No. 1, 1992 39

311+G**, and experimental values are all in close agreement, the largest discrepancy between theory and experiment being just 5 kJ mol^{-1} at MP4/6-311+G** and just 2 kJ mol^{-1} at G2. This lends confidence to our predicted heats of formation for the nitrogen analogues described above. We believe that the values given in Table III are the most reliable currently available for these nitrogen-containing systems.

Gas-Phase Acidities. Our calculations predict gas-phase acidities for ethynamine (Table II, reaction 3), ethenamine (reaction 5), and methylamine (reaction 17) of 1511, 1572, and 1694 kJ mol^{-1}, respectively. Thus, as for the ynol–enol–alcohol counterparts, ethynamine is predicted to be more acidic than ethenamine (in this case by 61 kJ mol^{-1}), and both the unsaturated amines are predicted to be more acidic than methylamine (by 183 and 122 kJ mol^{-1}, respectively) in the gas phase. The much greater acidity predicted for ethynamine compared with methylamine indicates that the strong acid-strengthening effect of the acetylenic linkage observed in aqueous solution carries over to the gas phase.

The calculated acidities for ethynamine and ethenamine may be compared with the acidities of ethynol and vinyl alcohol of 1390 and 1491 kJ mol^{-1}, where a difference of 101 kJ mol^{-1} was calculated.[3] Both the ynamine and enamine are calculated to be less acidic than their respective oxygen counterparts, as might have been expected for amines vs alcohols.

We turn now to the problem of providing a rationalization for the acidity ordering. A higher relative acidity implies relative stabilization of the neutral and/or relative destabilization of the anion. We can determine which of these factors operate in the case of the amine acidities by examining bond separation energies of appropriate reactions, e.g.

$$HC{\equiv}CX + CH_4 \rightarrow HC{\equiv}CH + CH_3X$$
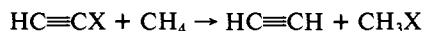
which provide a measure of the energies of interaction of a substituent X with double or (in the above example) triple bonds. Our calculated BSEs for ethynamine and ethenamine of 32 kJ mol^{-1} (reaction 7) and 50 kJ mol^{-1} (reaction 8), respectively, indicate small but favorable interactions of the NH_2 group with the multiple bond in both these neutral molecules. These interactions would contribute to acid-weakening rather than acid-strengthening effects.

The dominant effects occur in the ethynylamide ($HC{\equiv}CNH^-$, **10**) and ethenylamide ($CH_2{=}CHNH^-$, **5**) anions (which correspond to the conjugate bases of ethynamine and ethenamine) which show strong favorable interactions of the NH^- group and the multiple bonds, reflecting the benefits of charge delocalization. As a consequence, the bond separation energies are large and positive: 215 kJ mol^{-1} (reaction 9) and 172 kJ mol^{-1} (reaction 10). The greater stabilization of the anions compared with the neutral amines indicates immediately that both ethynamine and ethenamine are more acidic than methylamine, as shown diagrammatically in Figure 2.

In order to rationalize the greater acidity of ethynamine compared with ethenamine, we begin by noting (as pointed out previously[7,20]) that σ-electron withdrawal from a carbon–carbon triple bond is quite unfavorable, whereas π-electron donation is quite favorable. Carbon–carbon double bonds also benefit from π-electron donation but are much less sensitive than triple bonds to the σ effect of substituents. Because of the σ-electron-withdrawing nature of the NH_2 group, this leads to the less favorable interaction between the amine group and the triple bond of ethynamine (32 kJ mol^{-1}) than with the double bond of ethenamine (50 kJ mol^{-1}), corresponding to a relative destabilization of ethynamine compared with ethenamine of 18 kJ mol^{-1}.

For the anions, we note that the NH^- group is both a strong π-electron donor and a weak σ-electron donor. As a consequence, both σ and π interactions with the triple bond in ethynylamide
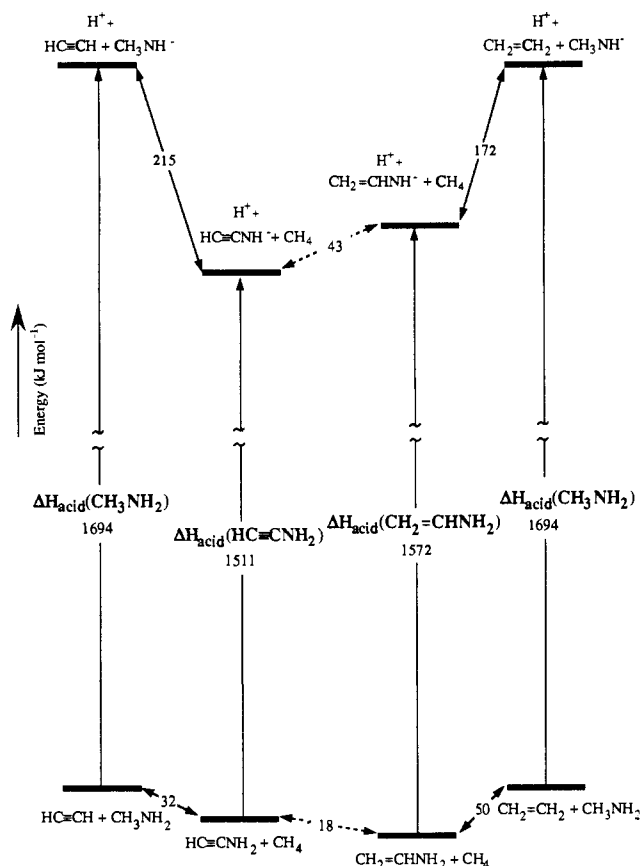

Figure 2. Schematic representation of calculated relative energies including calculated gas-phase acidities (ΔH_{acid}) (MP4/6-311+G** together with zero-point vibrational corrections).

anion ($HC{\equiv}CNH^-$, **10**) are favorable, leading to the calculated BSE (reaction 9) of 215 kJ mol^{-1}. Perhaps because of the decreased sensitivity of double bonds to the σ effect of substituents, we see for the ethenylamide anion ($CH_2{=}CHNH^-$, **5**) a smaller BSE of 172 kJ mol^{-1} (reaction 10). Thus, the $HC{\equiv}CNH^-$ anion (**10**) is relatively more stable than the $CH_2{=}CHNH^-$ anion (**5**) by 43 kJ mol^{-1}.

Both the relative destabilization of the neutral $HC{\equiv}CNH_2$ (**9**) (by 18 kJ mol^{-1}) and the relative stabilization of the anion $HC{\equiv}CNH^-$ (**10**) (by 43 kJ mol^{-1}) contribute to the greater acidity of $HC{\equiv}CNH_2$ (**9**) compared with $CH_2{=}CHNH_2$ (**4**) (by 61 kJ mol^{-1}).

Gas-Phase Basicities. We can make a similar type of analysis for the basicities of ethynamine, ethenamine, and methylamine. The calculated proton affinities (at nitrogen) are 795 kJ mol^{-1} (reaction 11), 864 kJ mol^{-1} (reaction 13), and 903 kJ mol^{-1} (reaction 18), respectively. Thus, we calculate that ethynamine is a substantially weaker (nitrogen) base (by 108 kJ mol^{-1}) than methylamine in the gas phase, as is found experimentally[1] for larger ynamine/amine systems in aqueous solution.

A lower relative basicity requires relative stabilization of the base and/or relative destabilization of the conjugate acid. Examination of Figure 3 shows that the dominant interaction influencing the basicity of ethynamine is a very strong (76 kJ mol^{-1}) destabilization of $HC{\equiv}CNH_3^+$ resulting from an unfavorable interaction of NH_3^+ with the triple bond (Table II, reaction 15). The latter may be attributed to the strong σ-electron-withdrawing and weak π-electron-donating properties of the NH_3^+ group. We have already noted the smaller stabilizing interaction (32 kJ mol^{-1}) of the NH_2 group with the triple bond in ethynamine itself. Both the stabilization of the base ($HC{\equiv}CNH_2$) and the destabilization of the conjugate acid ($HC{\equiv}CNH_3^+$) contribute to the 108 kJ mol^{-1} lower proton affinity of ethynamine compared with methylamine.

Ethenamine is also less basic than methylamine. In this case, the effect is much smaller (39 kJ mol^{-1}), the stabilization of the

(19) G2 energies were taken from ref 18, together with the following values (hartrees): acetaldehyde, -153.57682; vinyl alcohol, -153.55902; ketene, -152.36913; ethynol, -152.31363.

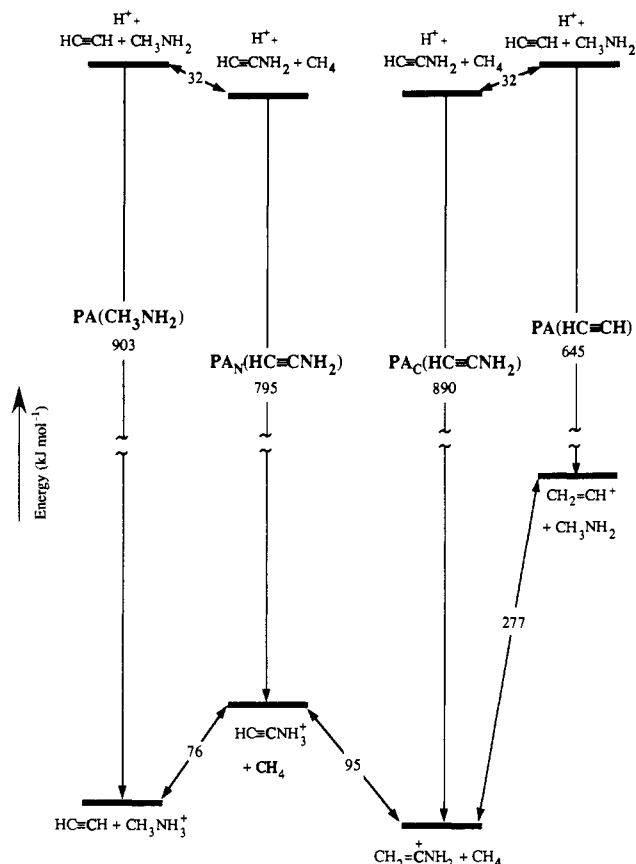(20) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 284.

Figure 3. Schematic representation of calculated relative energies including calculated gas-phase proton affinities (PA) for ethynamine and related systems (MP4/6-311+G** together with zero-point vibrational corrections).
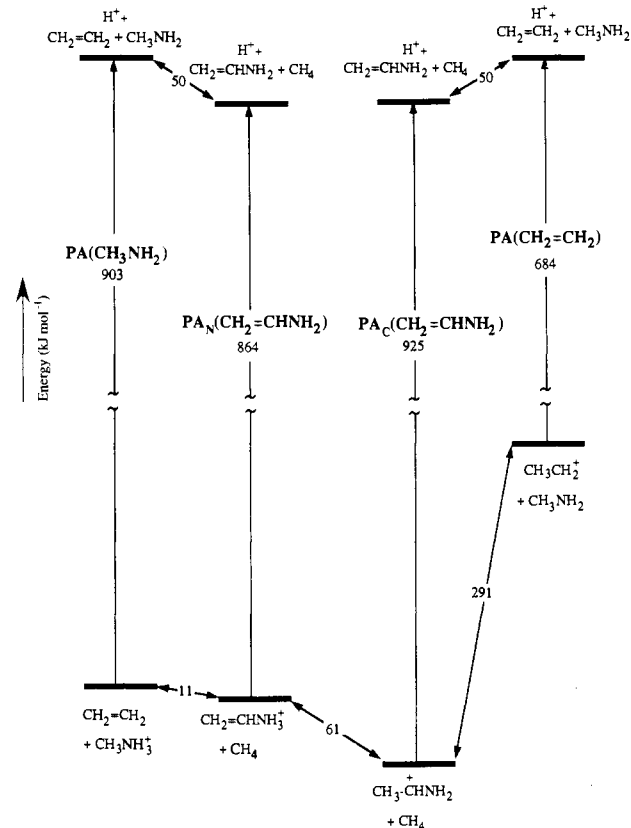
Figure 4. Schematic representation of calculated relative energies including calculated gas-phase proton affinities (PA) for ethenamine and related systems (MP4/6-311+G** together with zero-point vibrational corrections).

base (CH$_2$=CHNH$_2$, 4) by 50 kJ mol^{-1} being partly compensated by a stabilization by 11 kJ mol^{-1} of the conjugate acid (CH$_2$=CHNH$_3^+$, 2) (see Figure 4 and Table II, reaction 16).

The lower basicity of ethynamine compared with ethenamine must clearly be the result of destabilization of the ethynylammonium cation (HC≡CNH$_3^+$, 7) relative to the ethenylammonium cation (CH$_2$=CHNH$_3^+$, 2) since we have already seen that the neutral ethynamine is relatively *less* stable than ethenamine (by 18 kJ mol^{-1}). The strong (76 kJ mol^{-1}) unfavorable interaction of the triple bond with the NH$_3^+$ substituent in the ethynylammonium cation and the slight (11 kJ mol^{-1}) favorable interaction of the double bond with the NH$_3^+$ substituent in the ethenylammonium cation combine to make HC≡CNH$_3^+$ (7) relatively less stable than CH$_2$=CHNH$_3^+$ (2) by 87 kJ mol^{-1}. This is the major factor contributing to the 69 kJ mol^{-1} lower basicity of ethynamine than ethenamine.

Preferred Site of Protonation of Ynamines and Enamines. Since the proton affinity of methylamine is calculated to be greater than that of acetylene by some 258 kJ mol^{-1} (see Figure 3 and Table II, reactions 18 and 19), one might expect a strong preference for protonation of ethynamine on nitrogen rather than on carbon. However, our calculations, in agreement with the results of lower level theoretical calculations[21] and solution-phase experiments,[1] predict that the thermodynamically preferred site of protonation in ynamines is on carbon. Thus, CH$_2$=CNH$_2^+$ (6) lies lower in energy than HC≡CNH$_3^+$ (7) by 95 kJ mol^{-1}. How can this preference for protonation at carbon be explained?

The rationalization is included in Figure 3. The interactions within CH$_2$=CNH$_2^+$ are highly favorable, as reflected in the calculated bond separation energy of 277 kJ mol^{-1} (reaction 21,

Table II). In contrast, the interactions within HC≡CNH$_3^+$ are unfavorable by 76 kJ mol^{-1}. The combination of these two effects (353 kJ mol^{-1}) more than compensates for the intrinsically greater basicity of an NH$_2$ group compared with a C≡C triple bond (by 258 kJ mol^{-1}) to lead to a preference for carbon protonation by 95 kJ mol^{-1}.

Very similar considerations apply to the protonation of ethenamine, which has previously been studied in detail by Dixon, Farneth, and co-workers.[12-14,22] Their theoretical and gas-phase experimental studies show convincingly that enamines protonate exclusively at carbon rather than nitrogen. Our calculations show that the product arising from protonation at carbon (CH$_3$CHNH$_2^+$, 1) lies 61 kJ mol^{-1} lower in energy than the product arising from protonation at nitrogen (CH$_2$=CHNH$_3^+$, 2). This occurs despite the fact that the proton affinity of ethylene is much smaller (by 219 kJ mol^{-1}) than that for methylamine (Table II, reactions 18 and 22). Again, however, it is the favorable interactions within CH$_3$CHNH$_2^+$ (by the massive amount of 291 kJ mol^{-1}) (Table II, reaction 24) which leads to the apparent reversal of the preferred protonation site (Figure 4).

Conclusions

Several important points emerge from our theoretical study of the relative acidities and basicities of ethynamine, ethenamine, and methylamine: (1) Ethynamine has a very high relative acidity. This can be attributed largely to a relative stabilization of the ethynylamide anion. (2) Ethynamine has a very low relative basicity. This can be attributed largely to a relative destabilization of the ethynylammonium cation. (3) For both ethynamine and ethenamine, the preferred site of protonation is on carbon rather than on nitrogen. This can be attributed to strong stabilizing

(21) (a) Wurthwein, E.-U. *J. Org. Chem.* **1984**, *49*, 2971. (b) Nguyen, M. T.; Ha, T.-K. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1401. (c) DeFrees, D. J.; McLean, A. D.; Herbst, E. *Astrophys. J.* **1985**, *293*, 236.

(22) See also, Barone, V.; Lelj, F.; Grande, P.; Russo, N. *J. Mol. Struct. Theochem.* **1985**, *124*, 319.

interactions in the carbon-protonated species. (4) Our results are consistent with recent experimental findings for ynamines in aqueous solution.

Empirical Model Calculations for Thermodynamic and Structural Properties of Condensed Polycyclic Aromatic Hydrocarbons

William C. Herndon,* Paul C. Nowak, Dallas A. Connor, and Peiping Lin

Contribution from the Department of Chemistry, University of Texas at El Paso, El Paso, Texas 79968. Received May 6, 1991

Abstract: The majority of condensed polycyclic benzenoid aromatic hydrocarbons exist as highly nonplanar molecular structures. Group additivity methods, AM1 calculations, and molecular mechanics are compared as general tools for estimating relative and absolute stabilities in nonplanar members of this class of compounds and for correlating the sparse experimental ΔH_f° data. The AM1 computations give large, variable (positive) errors compared to the experimental ΔH_f°'s, whereas molecular mechanics and group additivity precisely model the same data. Molecular mechanics calculations for 153 polybenzenoid compounds with up to seven benzenoid rings indicate that 72 are highly nonplanar. The ability of group additivity methods to represent structural strain and the energetic consequences of nonplanarity in the polycyclic benzenoids is demonstrated by a precise partition of the calculated molecular mechanics ΔH_f° as a sum of CC and CH bond energy terms, steric interference parameters, and resonance energies.

1. Introduction

We are engaged in systematic studies of various classes of condensed polycyclic benzenoid aromatic hydrocarbons (PBAHs),[1,2] with an emphasis on understanding the effects of topological variations in structure on planarity, nonplanarity, and molecular stabilities. As part of this work, we have recently used a computerized coding system[3] and graph-theoretical algorithms to demonstrate that the majority of PBAHs capable of actual existence must possess highly nonplanar chiral and nonchiral molecular geometries.[4] Thus, for example, 6693 distinct polyhex graphs with ten rings can be drawn that correspond to catacondensed[5] PBAH constitutional isomers with the formula $C_{42}H_{24}$. However, easily perceived steric factors ensure that the $C_{42}H_{24}$ polybenzenoid system will actually consist of 12 882 nonplanar pairs of enantiomers, 47 achiral nonplanar species, and only 600 planar or near-planar compounds.[3]

Other than the graph-theory approach, the main tools for our studies have been AM1[6] and molecular mechanics[7] (MM) calculations. The reliance on computation is due primarily to the sparse amount of available experimental ΔH_f° data, which is limited to values for only nine catacondensed and two pericondensed compounds.[8,9] Therefore, in part, the work which is reported here was carried out to evaluate the general reliability and convenience of alternate and readily available theoretical protocols for obtaining the structural and thermodynamic properties of polybenzenoid systems.

The collected experimental information on thermodynamic stabilities is compared with the results of MM, AM1, and group additivity procedures in the following section of this paper. Then results of MM calculations for PBAHs with as many as seven rings are tabulated and discussed. Simple group additivity (GA) analyses are shown to provide acceptable replications of both the experimental and the theoretical thermodynamic data. The GA formalism also allows a delineation of the substructures which

Table I. Experimental and Calculated ΔH_f° (kcal/mol) for PBAHs

compd	exptl[a]	PCM[b]	MM3[c]	AM1[d]	GA1[e]	GARE[f]
benzene	20.0 (0.2)[g]	19.3	20.3	22.0	18.4	20.3
naphthalene	36.0 (0.3)	34.9	36.0	40.6	35.8	35.2
anthracene	55.2 (0.6)	55.6	55.2	62.9	53.3	53.8
phenanthrene	49.7 (0.6)	49.2	50.7	57.4	52.2	50.6
tetracene	72.3 (1.3)	78.2	76.2	86.9	70.8	74.1
benz[*a*]-anthracene	70.3 (0.9)	68.1	68.6	78.3	69.7	67.6
chrysene	66.0 (1.1)	65.9	67.0	76.2	68.5	67.1
triphenylene	66.5 (1.0)	66.9	67.5	75.5	67.3	67.1
benzo[*c*]-phenanthrene	69.6 (1.1)	69.3	71.8	81.2	69.6	69.6
pyrene	54.0 (0.3)	57.4	58.2	67.4	58.6[g]	55.3[h]
perylene	78.4 (0.6)	79.3		89.3	73.8[g]	77.2[h]
av error (exptl vs calc)		1.4	1.5	9.1	1.9	1.1

[a] Reference 14. [b] Reference 10. [c] Reference 11. [d] Reference 6. [e] Based on a five parameter group additivity equation. See Table II. [f] Group additivity models with a resonance energy parameter (GA2-(RE) and GA3(RE)) give essentially identical predicted ΔH_f°. See text and Table II. [g] Estimated absolute value of experimental error. See ref 14. [h] Experimental and estimated ΔH_f°'s modified by energy/enthalpy correction term. See text.

induce both small and large degrees of nonplanarity in PBAH molecular frameworks.

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* Author to whom correspondence should be addressed.