Heats of formation for the azine series: A Gaussian-3 study

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Applying the Gaussian-3 (G3) model and its variant G3(MP2), and using the atomization scheme, the heats of formation (ΔH_f) at 0 K and 298 K have been calculated for twelve monocyclic azines with the general formula $N_n(CH)_{6-n}$, $n = 1, 2, \ldots, 6$. Upon comparing the calculated results with available experimental data, it is found that the calculated structural parameters agree very well with the experimental ones. Additionally, most of the calculated ΔH_f values are well within ± 10 kJ mol^{-1} of the available experimental data. Thus, it is concluded that the unfavorable accumulation of component errors found in the Gaussian-2 methods is greatly reduced in the G3 models. Also, the calculated ΔH_f values for those azines for which no experimental data exists should be reliable estimates.

Keywords: azines, heats of formation, Gaussian-3 calculation.

INTRODUCTION

Azines are six-membered heterocyclic compounds with the general formula, $N_n(CH)_{6-n}$, with $n = 1, 2, \ldots, 6$. This series of compounds ranges from the very familiar pyridine to the heretofore unknown pentazine (N_5CH) and hexazine (N_6). In addition, members of this series exhibit interesting chemistry. For instance, the Diels-Alder reactions between unsubstituted and phenyl-substituted acetylenes and 1,2,4,5-tetrazines have been studied experimentally and computationally.[1] Furthermore, substituted dialkyl-amino 2,4-triazines constitute a family of compounds with herbicidal activity. They also inhibit photosynthetic electron flow in higher plants.[2]

In our previous works,[3,4] the heats of formation at 0 K (ΔH_{f0}) and at 298 K (ΔH_{f298}) were calculated using Gaussian-2 (G2)[5] and Gaussian-3 (G3)[6] based methods. In an earlier report,[3] it was found that the G2 methods suffer "an unfavorable accumulation of component small errors". Furthermore, this shortcoming may be circumvented using isodesmic reactions in the computation scheme. On the other hand, in a more recent report,[4] it was found that the aforementioned error accumulation is significantly reduced in the G3 methods and hence the ΔH_f values of molecules with the size

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of benzene may be calculated directly, *i.e.,* using the atomization scheme. This result is important, as, for some compounds, isodesmic reactions cannot always be written readily.

TABLE I. Total energies (in hartrees) at 0 K (E_0) and enthalpies at 298 K (H_{298}) for the azines studied in this work calculated at the G3 and G3(MP2) levels

Azine	E_0		H_{298}	
	G3	G3(MP2)	G3	G3(MP2)
1	–248.09290	–247.86761	–248.08759	–247.86230
2a	–264.10064	–263.87320	–264.09542	–263.86798
2b	–264.13679	–263.90868	–264.13160	–263.90350
2c	–264.12963	–263.90195	–264.12446	–263.89678
3a	–280.11543	–279.88569	–280.11029	–279.88054
3b	–280.14086	–279.91089	–280.13577	–279.90580
3c	–280.18390	–279.95312	–280.17884	–279.94806
4a	–296.12560	–295.89395	–296.12050	–295.88885
4b	–296.14664	–295.91486	–296.14160	–295.90982
4c	–296.15830	–295.92601	–296.15326	–295.92096
5	–312.13765	–311.90400	–312.13253	–311.89889
6	–328.12095	–327.88608	–328.11544	–327.88057

In the present work, the ΔH_f values of twelve azines were calculated using the G3 method, as well as a variant of this method, G3(MP2).[7] The purpose of these calculations is twofold. First, by comparing the calculated results with available experimental data, the relative merits of these G3 methods can be assessed. Second, if the G3 methods prove to be trustworthy, the calculated ΔH_f results for those azines for which no experimental data exists should be reliable estimates.

METHODS OF CALCULATION AND RESULTS

All calculations were carried out on various workstations using the Gaussian 98 package of programs.[8] The methods of calculation employed, G3 and G3(MP2), are briefly described below.

In the G3 method, geometry optimization is carried out at the MP2(Full)/6-31G(d) level. To determine the energy E_e of a structure, single-point calculations at the levels of QCISD(T)/6-31G(d), MP4/6-31G(d), MP4/6-31+G(d), MP4/6-31G(2df,p), and MP2(Full)/G3large are carried out. In addition, higher-level correction (HLC) is applied in the calculation of E_e. The HF/6-31G(d) vibrational frequencies, scaled by 0.8929, are applied for the zero-point vibrational energy (ZPVE) correction at 0 K ($E_0 = E_e + $ ZPVE). In the G3(MP2) model, again based on the geometry optimized at the MP2(Full)/6-31G(d) level, frozen-core single-point calculations (QCISD(T)/6-31G(d) and MP2/G3MP2large are carried out. Also, HLC and ZPVE corrections are applied. The error bar of these methods for systems with the size of azines is expected to be about ±10 kJ mol⁻¹.
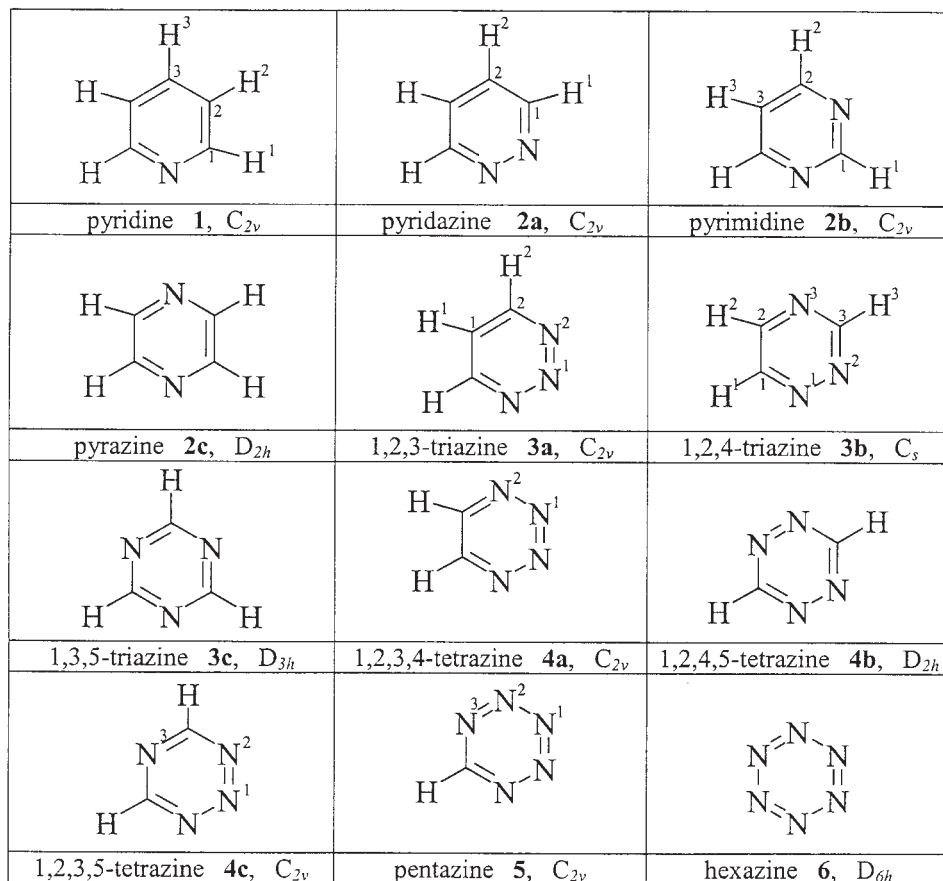
Fig. 1. The molecular structures and labeling of the atoms for the twelve $N_n(CH)_{6-n}$, n = 1–6, isomers studied in this work.

Table I lists the total energies at 0 K (E_0) and enthalpies at 298 K (H_{298}) for the azines calculated at the G3 and G3(MP2) levels. To convert these results into ΔH_f values for the azines using the so-called atomization scheme,[3,4,9] the experimental[10] ΔH_{f0} values of C (711.2 kJ mol^{-1}), H (216.0 kJ mol^{-1}), and N (470.8 kJ mol^{-1}), as well as the experimental[10] ΔH_{f298} values of C (716.7 kJ mol^{-1}), H (218.0 kJ mol^{-1}), and N (472.7 kJ mol^{-1}) are required. The G3 and G3(MP2) heats of reactions at 0 K and 298 K for the azines are summarized in Table II, along with available experimental data for ready comparison.

The structural parameters of the azines, optimized at the MP2(Full)/6-31G(d) level, are summarized in Table III. Also included in this Table are the available experimental structural data, as well as those calculated at other theoretical levels. The molecular structures and labeling of the atoms for the azines are shown in Fig. 1.

TABLE II. Heat of formation (kJ mol^{-1}) at 0 K (ΔH_{f0}) and 298 K (ΔH_{f298}) for the studied azines calculated with the G3 and G3(MP2) methods

Azine	ΔH_{f0}[a]		ΔH_{f298}[b]		
	G3	G3(MP2)	G3	G3(MP2)	Experimental[c]
1	157.8	153.7	143.0	138.9	140±1
2a	299.7	297.1	285.3	282.6	278.3±1
2b	204.8	203.9	190.3	189.3	196.6±0.9
2c	223.6	221.6	209.0	207.0	196.0±1.3
3a	423.1	422.3	409.1	40.8.2	416
3b	356.3	356.1	342.2	341.9	334
3c	243.4	245.2	229.1	231.0	226±1
4a	558.6	558.6	545.1	545.0	
4b	503.4	503.7	489.7	489.9	464[d]
4c	472.8	474.4	459.1	460.7	
5	689.2	690.2	676.3	677.2	
6	895.3	895.2	884.0	883.9	

[a]To obtain these ΔH_{f0} values, in addition to the E_0 values given in Table I, the E_0 values of the constituent atoms were also required. At the G3 level, the E_0 values for C, H and N are –37.82772, –0.50100, and –54.56434 hartrees, respectively. At the G3(MP2) level, the corresponding values are –37.78934, –0.50184, and –54.52519 hartrees.
[b]To obtain these ΔH_{f298} values, in addition to the H_{298} values listed in Table I, the ΔH_{f298} values for the constituent atoms were also required. These quantities can be obtained by adding $E_{\text{trans}} + PV (= 2.4RT = 0.00236$ hartrees at 298 K) to the atomic E_0 values.
[c]Taken from Ref. 10.
[d]See discussion in text.

DISCUSSION

First the structural data listed in Table III is examined. Five azines, pyridine (**1**), pyridazine (**2a**), pyrimidine (**2b**), pyrazine (**2c**), and 1,3,5-triazine (**3c**), have experimental structural data[11,12] available in the literature. Upon comparing these data with our calculated results, it can be seen that the agreement ranges from good to excellent. The only relatively poor agreement occurs for the C^{2}C^2 bond in **2a**: 1.385 Å *vs.* 1.375 Å. Also, it is not surprising that calculations at the MP2/6-311G(d,p) level for **2a** yield slightly better results.[1] On the other hand, theoretical results for **3c** at the MP2/cc-pVTZ level are very similar to ours. Finally, it is noted that hexazine (**6**) was reportedly observed in a matrix about twenty years ago,[13] which inspired a number of theoretical studies.[14]

Attention is now turned to the energetics results. Examining Table II, is seen that only the experimental heats of formation at 298 K of some azines are available for comparison, while there are no experimental ΔH_{f0} values for azines to be found in the literature. Comparing the G3 and G3(MP3) ΔH_{f298} values with their experimental counterparts, it is seen that most of the agreements are well within ±10 kJ mol^{-1}, the expected

error range for these two theoretical methods. The only obvious exception is the difference between the calculated and experimental ΔH_{f298} values for 1,2,4,5-tetrazine (**4b**), which is about 25 kJ mol^{-1}. Upon further checking of the literature, it was found that the "experimental" ΔH_{f298} for **4b**, 464 kJ mol^{-1} or 111 kcal mol^{-1}, was "predicted" by adding the bond ΔH_f values in the following manner:[15] 2×35.3 kcal mol^{-1} (ΔH_f for N – N) + 4×13.5 kcal mol^{-1} (ΔH_f for C – N) + 2±(–6.8 kcal mol^{-1}) (ΔH_f for C – H). Obviously, in view of the accuracy of the G3 results for the other azines, there is no reason to believe that the value predicted for **4b** by such a simple additivity rule should be more reliable than the G3 results. Finally, for pyrazine (**2c**), the G3(MP2) and G3 ΔH_{f298} values (207.7 and 209.0 kJ mol^{-1}, respectively) may be considered as barely within 10 kJ mol^{-1} of the experimental result (196.0±1.3 kJ mol^{-1}).

TABLE III. Calculated structural parameters (in Å and degrees) optimized at the MP2(Full)/6-31G(d) level of the azines studied in this work

Parameter	Calculated	Experimental	Other	Parameter	Calculated	Experimental	Other
Pyridine **1**				Pyrimidine **2b**			
NC^1	1.344	1.338[a]		C^{1}N	1.340	1.340[a]	
C^{1}C^2	1.394	1.394[a]		NC^2	1.342	1.350[a]	
C^{2}C^3	1.393	1.392[a]		C^{2}C^3	1.391	1.410[a]	
C^{1}H^1	1.088	1.083[a]		H^{1}C^1	1.087		
C^{2}H^2	1.086	1.083[a]		H^{2}C^2	1.088		
C^{3}H^3	1.087	1.082[a]		H^{3}C^3	1.085		
C^{1}NC^1	116.8	116.9[a]		NC^{1}N	127.4	129.7[a]	
NC^{1}C^2	123.8	123.8[a]		C^{1}NC^2	115.6	115.0[a]	
C^{1}C^{2}C^3	118.6	118.5[a]		NC^{2}C^3	122.3	121.3[a]	
C^{2}C^{3}C^2	118.4	118.5[a]		C^{2}C^{3}C^2	116.8	118.6[a]	
H^{1}C^{1}C^2	120.5			H^{1}C^{1}N	116.3		
H^{2}C^{2}C^3	121.1			H^{2}C^{2}N	116.2		
H^{3}C^{3}C^2	120.8			H^{3}C^{3}C^2	121.5		
Pyridazine **2a**				Pyrazine **2c**			
NN	1.347	1.330[a]	1.340[b]	NC	1.343	1.339[a]	
NC^1	1.343	1.341[a]	1.341[b]	CC	1.394	1.393[a]	
C^{1}C^2	1.396	1.393[a]	1.398[b]	HC	1.088		
C^{2}C^2	1.385	1.375[a]	1.367[b]	CNC	115.4	116.3[a]	
C^{1}H^1	1.087		1.075[b]	NCC	122.3	121.8[a]	
C^{2}H^2	1.086		1.075[b]	HCN	116.6		
NNC^1	119.0	119.3[a]					
NC^{1}C^2	124.0	123.7[a]					
C^{1}C^{2}C^2	117.0	117.1[a]					
H^{1}C^{1}N	114.4						
H^{2}C^{2}C^2	122.1						

TABLE III. Continued

Parameter	Calculated	Experimental	Other	Parameter	Calculated	Experimental	Other
1,2,3-Triazine **3a**				1,2,3,4-Tetrazine **4a**			
N^1N^2	1.340			N^1N^1	1.335		
N^2C^2	1.345			N^1N^2	1.346		
C^1C^2	1.387			N^2C	1.337		
H^1C^1	1.085			CC	1.390		
H^2C^2	1.087			HC	1.086		
$N^2N^1N^2$	121.0			$N^1N^1N^2$	121.6		
$N^1N^2C^2$	119.7			N^1N^2C	117.8		
$N^2C^2C^1$	122.2			N^2CC	120.6		
$C^2C^1C^2$	115.2			HCN^2	116.3		
$H^1C^1C^2$	122.3			1,2,4,5-Tetrazine **4b**			
$H^2C^2N^2$	115.1			NN	1.339		1.333[b]
1,2,4-Triazine **3b**				CN	1.344		1.341[b]
N^1N^2	1.346			HC	1.085		1.084[b]
N^2C^3	1.340			NNC	116.4		
C^3N^3	1.345			NCN	127.2		
N^3C^2	1.335			HCN	116.4		
C^1C^2	1.395			1,2,3,5-Tetrazine **4c**			
C^1N^1	1.340			N^1N^2	1.337		
H^1C^1	1.086			N^2C	1.342		
H^2C^2	1.087			CN^3	1.336		
H^3C^3	1.086			HC	1.086		
$C^1N^1N^2$	117.6			$N^2N^1N^2$	119.7		
$N^1N^2C^3$	118.0			N^1N^2C	118.2		
$N^2C^3N^3$	127.4			N^2CN^3	125.6		
$C^3N^3C^2$	114.1			CN^3C	112.7		
1,3,5-Triazine **3c**				HCN^3	118.1		
NC	1.339	1.338[c]	1.335[c]	Pentazine **5**			
HC	1.087	1.084[c]	1.082[c]	N^1N^2	1.340		
CNC	114.0	113.2[c]	114.1[c]	N^2N^3	1.336		
NCN	126.0	126.8[c]	126.0[c]	N^3C	1.338		
HCN	117.0	116.6[c]	117.0[c]	HC	1.085		
$N^3C^2C^1$	120.7			$N^2N^1N^2$	121.8		
$C^2C^1N^1$	122.2			$N^1N^2N^3$	119.8		
$H^1C^1N^1$	115.5			N^2N^3C	116.6		
$H^2C^2N^3$	117.4			N^3CN^3	125.4		
$H^3C^3N^3$	117.1			HCN^3	117.3		
				Hexazine **6**			
				NN	1.337[d]		1.337[e]

[a]Ref. 11. [b]Ref. 1. [c]Ref. 12.; [d]Parameter optimized at the HF/6-31G(d) level; [e]Ref. 14

CONCLUSION

The heats of formation of twelve monocyclic azines with the general formula $N_n(CH)_{6-n}$, $n = 1,2,…,6$, have been calculated using the G3 and G3(MP2) models of theory. Upon examining the results, it is found that the geometrical parameters optimized at the MP2(Full)/6-31G(d) level are, in general, in very good agreement with the experimental ones. Also, most of the calculated ΔH_{f298} values are well within ±10 kJ mol^{-1} of the experimental data. Hence, it may once again be concluded that the unfavorable accumulation of component errors found in G2-based methods has been markedly reduced in G3 methods. Also, the G3 results for those azines for which no experimental data exists should be reliable estimates. Finally, it is pointed out that G3 and G3(MP2) methods yield very comparable results for azines, even though the more elaborated G3 model gives slightly better results for some members of the series. Hence, if computation resource limitation is a factor, the G3(MP2) model is a dependable substitute for the G3 method.

И З В О Д

ТОПЛОТЕ СТВАРАЊА СЕРИЈЕ АЗИНА: СТУДИЈА ПОМОЋУ Gaussian-3 МОДЕЛА

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Применом модела Gaussian-3, и његове варијанте G3(MP2), као и схеме атомизације, израчунате су топлоте стварања (ΔH_f) на 0 K и 298 K за 12 моноцикличних азина опште формуле $N_n(CH)_{6-n}$, $n = 1,2,…,6$. Поређењем израчунатих и доступних експерименталних података нађено је врло добро слагање, при чему су израчунате вредности ΔH_f у границама ±10 kJ mol^{-1} у односу на доступне експерименталне вредности. На основу овога је закључено да је неповољно нагомилавање компонентних грешака које се јавља код методе Gaussian-2 у случају G3 модела значајно редуковано. Такође, израчунате вредности ΔH_f за азине за које не постоје експерименталне вредности могу се узети као поуздане процене.

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