The Heats of Formation of Diazene, Hydrazine, $N_2H_3^+$, $N_2H_5^+$, N_2H, and N_2H_3 and the Methyl Derivatives CH_3NNH, CH_3NNCH_3, and $CH_3HNNHCH_3$

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The heats of formation of N_2H, diazene (*cis*- and *trans*-N_2H_2), N_2H_3, and hydrazine (N_2H_4), as well as their protonated species (diazenium, $N_2H_3^+$, and hydrazinium, $N_2H_5^+$), have been calculated by using high level electronic structure theory. Energies were calculated by using coupled cluster theory with a perturbative treatment of the triple excitations (CCSD(T)) and employing augmented correlation consistent basis sets (aug-cc-pV*n*Z) up to quintuple-ζ, to perform a complete basis set extrapolation for the energy. Geometries were optimized at the CCSD(T) level with the aug-cc-pVDZ and aug-cc-pVTZ basis sets. Core-valence and scalar relativistic corrections were included, as well as scaled zero point energies. We find the following heats of formation (kcal/mol) at 0 (298) K: $\Delta H_f(N_2H) = 60.8$ (60.1); $\Delta H_f(cis\text{-}N_2H_2) = 54.9$ (53.2); $\Delta H_f(trans\text{-}N_2H_2) = 49.9$ (48.1) versus $\geq 48.8 \pm 0.5$ (exptl, 0 K); $\Delta H_f(N_2H_4) = 26.6$ (23.1) versus 22.8 ± 0.2 (exptl, 298 K); $\Delta H_f(N_2H_3) = 56.2$ (53.6); $\Delta H_f(N_2H_3^+) = 231.6$ (228.9); and $\Delta H_f(N_2H_5^+) = 187.1$ (182.7). In addition, we calculated the heats of formation of CH_3NH_2, CH_3NNH, and $CH_3HNNHCH_3$ by using isodesmic reactions and at the G3(MP2) level. The calculated results for the hydrogenation reaction $RNNR + H_2 \rightarrow RHNNHR$ show that substitution of an organic substituent for H improved the energetics, suggesting that these types of compounds may be possible to use in a chemical hydrogen storage system.

Introduction

We have been exploring the thermodynamics of various compounds that could be used in chemical hydrogen storage systems either as compounds themselves or as intermediates in various approaches to store H_2 in a chemical compound for use in the transportation sector. We have been using high level ab initio molecular orbital theory to predict the heats of formation of relevant compounds based on an approach developed over a number of years at the Pacific Northwest National Laboratory. For example, we have studied borane amines[1] as well as related ioselectronic species[2] and carbenes.[3] We are interested in organic derivatives of diazene or diimide (N_2H_2) and hydrazine (N_2H_4) as potential hydrogen storage systems based on cyanocarbon chemistry. For example, we are interested in the following generic reaction for different R groups:

$$N_2R_2 + H_2 \leftrightarrow N_2R_2H_2 \qquad (1)$$

We need to be able to predict the energetics for these species as well as for the addition of a proton to them and for the loss of H (breaking an N−H bond). We have already reported high level calculations on the various NH_x species, $x = 1$ to 3, and found excellent agreement with experiment.[4] Our goal is to be able to predict the heats of formation of these compounds and then to use these results to develop heats of formation of larger organic derivatives based on isodesmic reactions.

Diazene is the prototypical azo-compound and its different isomers have been studied by using coupled cluster methods with large basis sets.[5,6] Martin and Taylor used basis sets up through aug-cc-pV5Z to predict the heat of formation to be 49.2 ± 0.3 kcal/mol at 0 K at the CBS limit by using a calculated anharmonic force field[7] and including core-valence correlation corrections. This is in excellent agreement with the experimental value of $\geq 48.8 \pm 0.5$ kcal/mol.[8] They also calculated the cis−trans isomerization energy to be 5.2 ± 0.2 kcal/mol at 0 K.

In recent years, computational approaches based on ab initio electronic structure theory have been used to reevaluate the heats of formation in small molecules in order to improve the accuracy of these values. We have used a composite theoretical approach, based on ab initio molecular orbital theory, in which empirical parameters are not included, except when necessary for spin−orbit energies in atoms and in calculating zero point energies.[9,10] Our approach is based on calculating the total atomization energy (TAE) of a molecule to obtain heats of formation at 0 K utilizing the known heats of formation of the atoms. The TAE is calculated by using coupled cluster theory, including a perturbative treatment of the triple excitations (CCSD(T))[11−13] combined with augmented correlation-consistent basis sets[14,15] extrapolated to the complete basis set (CBS) limit to treat the correlation energy of the valence electrons. Corrections, such as core-valence interactions and relativistic effects, and the zero point energy (ZPE), obtained either from a combination of experiment and theory or from theoretical scaled values, are also included. The standard heats of formation of compounds at 298 K can then be calculated by using standard thermodynamic and statistical mechanics expressions.[16]

We have used such an approach to calculate the heats of formation of N_2H_2, N_2H_4, N_2H_3, N_2H, diazenium ($N_2H_3^+$), and hydrazinium ($N_2H_5^+$). In addition, we calculated the heats of formation at the G3(MP2) level.[17] We have also calculated the heats of formation of RNNH, RNNR, and RHNNHR for R = CH_3 by using an isodesmic reaction approach at the density functional theory level[18] with the B3LYP exchange-correlation functional[19] and at the MP2/CBS level as well as by direct

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calculation at the G3(MP2) level. These values are then used to assess the hydrogenation energy of reaction 1 for R = CH_3.

Computational Approach

The augmented correlation consistent basis sets aug-cc-pV*n*Z (n = D, T, Q, 5) were used for most of the calculations,[20] and, for brevity, the basis set names are shortened to aV*n*Z. All of the current work was performed with the Gaussian03[21] and MOLPRO[22] programs.

We first describe highly accurate calculations based on the CCSD(T)/CBS extrapolations. The geometries were optimized at the frozen core CCSD(T) level by using the aVDZ and aVTZ basis sets. This level of calculation was also employed for the prediction of the harmonic vibrational frequencies of N_2H (nonlinear, C_s symmetry), N_2H_2 (cis and trans isomers), N_2H_4, and their protonated species. For N_2H_3, the geometry and frequencies were calculated at the CCSD(T)/aVDZ level. We could not get the frequency calculations to converge for linear N_2H ($C_{\infty v}$ symmetry), so the frequencies for this transition state were calculated with the B3LYP exchange-correlation functional at the density functional theory level.

For *trans*-N_2H_2 and N_2H_4, the calculated harmonic frequencies were averaged with the corresponding experimental values to calculate the ZPE correction.[23] For *trans*-N_2H_2, Martin and Taylor[6] find a ZPE of 17.53 kcal/mol and our value is 17.42 kcal/mol suggesting that our approach will introduce a maximum error of ±0.4 kcal/mol for the compounds with more hydrogens. For the remaining molecules, there are no experimental values so the ZPEs were scaled by a factor obtained from the ratio of the averaged ZPE from a molecule with experimental values and the theoretical ZPE from the same molecule. For *cis*-N_2H_2, N_2H, and $N_2H_3^+$, the ZPEs were scaled by 0.983, obtained from the ratio of the averaged ZPE and the CCSD(T)/aVTZ ZPE values for *trans*-N_2H_2. For the *cis*-N_2H_2 isomer, Martin and Taylor obtain a ZPE of 17.15 kcal/mol and we obtain 17.03 kcal/mol. For N_2H_3 and $N_2H_5^+$, the scaling factor is 0.987 from the ratio of the averaged ZPE and the CCSD(T)/aVTZ ZPE values for N_2H_4.

The CCSD(T)/aVTZ geometries were used in single point CCSD(T)/aVQZ and CCSD(T)/aV5Z calculations. The CCSD(T) total energies were extrapolated to the CBS limit by using a mixed exponential/Gaussian function of the form

$$E(n) = E_{\mathrm{CBS}} + A\exp[-(n-1)] + B\exp[-(n-1)^2] \quad (2)$$

with n = 2 (aVDZ), 3 (aVTZ), and 4 (aVQZ), as proposed by Peterson et al.[24] We also used the following expansion in $1/l_{\max}$,[25] where $l_{\max}$ equals the highest angular momentum present in the basis set, to estimate the complete basis set limit using the aVQZ and aV5Z results:

$$E(l_{\max}) = E_{\mathrm{CBS}} + B/l_{\max}^{\ 3} \quad (3)$$

The use of expressions 2 and 3 provides insight into the extrapolation error. The CCSD(T) calculations for open-shell atoms and molecules were carried out at the R/UCCSD(T) level. In this approach, a restricted open shell Hartree−Fock (ROHF) calculation was initially performed and the spin constraint was relaxed in the coupled cluster calculation.[26−28]

Core-valence corrections, ΔE_{CV}, were obtained at the CCSD(T)/cc-pwCVTZ level.[29] Scalar relativistic corrections, ΔE_{SR}, which account for changes in the relativistic contributions to the total energies of the molecule and the constituent atoms, were included at the CI-SD (configuration interaction singles and doubles) level of theory by using the aug-cc-pVTZ basis set. ΔE_{SR} is taken as the sum of the mass-velocity and 1-electron Darwin (MVD) terms in the Breit−Pauli Hamiltonian.[30] For these species, there is no spin−orbit correction in the atoms.

TABLE 1: Comparison of Calculated Bond Lengths (Å) and Angles (deg) with Experimental Values

molecule	method	r_{NN}	r_{NH}	∠NNH	∠HNNH
N_2	CCSD(T)/aVDZ	1.1209			
	CCSD(T)/aVTZ	1.1040			
	exptl[a]	1.0977			
NH_3	CCSD(T)/aVTZ		1.0237	105.9[g]	112.2[h]
	CCSD(T)/aVTZ		1.0149	106.40[g]	113.20[h]
	exptl[b]		1.0116	106.7[g]	113.7[h]
N_2H (C_s)	CCSD(T)/aVDZ	1.1986	1.0607	115.60	
	CCSD(T)/aVTZ	1.1830	1.0517	116.44	
N_2H ($C_{\infty v}$)	CCSD(T)/aVDZ	1.1969	1.0079	180.00	
	CCSD(T)/aVTZ	1.1820	0.9982	180.00	
cis-N_2H_2	CCSD(T)/aVDZ	1.2652	1.0464	111.57	0.0
	CCSD(T)/aVTZ	1.2526	1.0365	111.77	0.0
trans-N_2H_2	CCSD(T)/aVDZ	1.2659	1.0415	105.75	180.0
	CCSD(T)/aVTZ	1.2528	1.0318	106.13	180.0
	CCSD(T)[c]	1.2468	1.0281	106.17	
	exptl[d]	1.247	1.029	106.3	
N_2H_3	MP2/aVDZ	1.3496	1.0275	105.53	
			1.0132	113.91	167.84
			1.0171	120.86	23.97
	MP2/aVTZ	1.3393	1.0186	105.82	
			1.0056	114.21	168.11
			1.0092	120.93	22.92
	CCSD(T)/aVDZ	1.3683	1.0334	105.82	
			1.0170	112.45	165.47
			1.0210	119.00	29.02
$N_2H_3^+$	CCSD(T)/aVDZ	1.2476	1.0422	109.66	
			1.0330	116.95	180.00
			1.0359	124.53	0.00
	CCSD(T)/aVTZ	1.2346	1.0334	110.20	
			1.0260	117.13	180.00
			1.0286	124.46	0.00
N_2H_4	CCSD(T)/aVDZ	1.4559	1.0222	106.15	154.58
			1.0252	110.85	−90.13
	CCSD(T)/aVTZ	1.4448	1.0130	106.63	153.79
			1.0162	111.13	−89.73
	exptl[e]	1.447(5)	1.008(8)	109.2(8)	88.9(15)
	exptl[f]	1.447(2)	1.015(2)	106(2)	91(2)
				112(2)	
$N_2H_5^+$	CCSD(T)/aVDZ	1.4605	1.0332	116.20	
			1.0288	107.31	±122.60
			1.0288	107.31	±57.39
	CCSD(T)/aVTZ	1.4509	1.0266	115.85	
			1.0212	107.56	±122.42
			1.0212	107.56	±57.94

[a] Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure Constants of Diatomic Molecules*; Van Nostrand-Reinhold: New York, 1979. [b] Duncan, J. L.; Mills, I. M. *Spectrochim. Acta* **1964**, *20*, 523. [c] Reference 5, CCSD(T)/cc-pvQZ+CCSD(T)/MTcore-CCSD(T)/MTnocore. [d] Reference 35. [e] ref 36a, microwave. [f] Reference 36b, microwave and electron diffraction. [g] ∠HNH. [h] ∠HNHH.

The dissociation energy ($\sum D_0$ or TAE) of a compound is given by the expression:

$$\sum D_0 = \Delta E_{\mathrm{elec}}(\mathrm{CBS}) - \Delta E_{\mathrm{ZPE}} + \Delta E_{\mathrm{CV}} + \Delta E_{\mathrm{SR}} \quad (4)$$

By following the procedures by Curtiss et al.,[16] we can obtain gas phase heats of formation at 298 K from our computed $\sum D_0$ values and the known heats of formation at 0 K for the elements ($\Delta H_f^{\,0}(\mathrm{N}) = 112.53$ kcal/mol and $\Delta H_f^{\,0}(\mathrm{H}) = 51.63$ kcal/mol).[31]

For the molecules with R = CH_3, the geometries were optimized at the B3LYP/aVTZ level and frequencies for zero point and thermal corrections were also obtained at this level. MP2 calculations[32] were done with this geometry with the aV*n*Z basis sets n = D, T, and Q, and extrapolated to the CBS limit

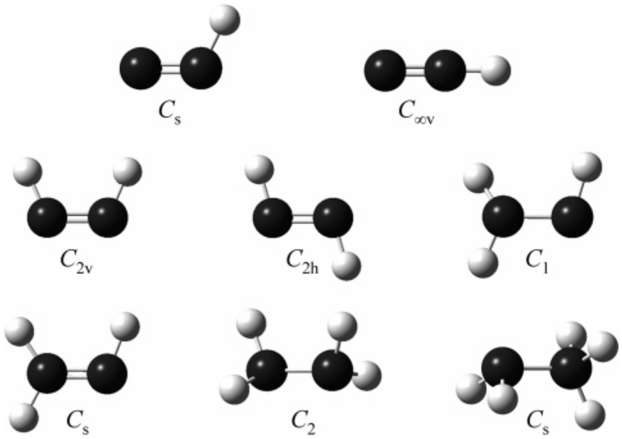

Figure 1. Optimized molecular structures and their symmetry point group for NH_2 (nonlinear), NH_2 (linear), *cis*-N_2H_2, *trans*-N_2H_2, N_2H_3, $N_2H_3^+$, N_2H_4, and $N_2H_5^+$.

by using eq 2. We then used the following isodesmic reactions to calculate the heats of formation.

$$CH_3NH_2 + N_2H_2 \rightarrow CH_3NNH + NH_3 \qquad (5)$$

$$2CH_3NH_2 + N_2H_2 \rightarrow CH_3NNCH_3 + 2NH_3 \qquad (6)$$

$$2CH_3NH_2 + N_2H_4 \rightarrow CH_3HNNHCH_3 + 2NH_3 \qquad (7)$$

We also calculated the isodesmic reaction energies at the DFT level with the B3LYP functional[19] and the DZVP2[33] and 6-311++G**[34] basis sets. In addition, all of the heats of formation were calculated with the G3(MP2) approach.[17]

Results and Discussion

The geometry parameters of the N_2H_x compounds are given in Table 1 and the geometries and point group symmetries for the different species are shown in Figure 1. For *trans*-N_2H_2, the geometry is in good agreement with the best computational values[6,7] as well as the experimental values[35] within 0.005 Å with the aVTZ basis set. For N_2H_4, there is similar good agreement with experiment[36] for the aVTZ geometry. The bond distance in N_2H_4 is much longer than the bond distance in N_2H_2 consistent with the nominal single bond character in the former and the nominal double bond character in the latter.

The geometry of N_2H is predicted to be bent as would be expected and has $^2A'$ symmetry. The linear structure is predicted to be a transition state for inverting the ∠NNH and is 27.2 kcal/mol higher in energy at the CCSD(T)/CBS level. The geometry of N_2H shows an N−H bond elongated from that in *trans*-N_2H_2 and an N−N bond that is shorter than that in N_2H_2 by 0.07 Å but longer than that in N_2 by 0.08 Å at the aVTZ level. $N_2H_3^+$ is similar to N_2H_2 in that it has a reasonably short N−N bond. The molecule is planar and the short N−N bond is consistent with this as the molecule can be considered to be an amine

TABLE 2: Calculated and Experimental Vibrational Frequencies (cm^{-1})[a]

molecule	symmetry	aVDZ	aVTZ	exptl
N_2	σ_g	2318.3	2339.6	2331[b] ($\omega_e = 2358.6$)
NH_3	a_1		1063.7	950[c]
	e		1671.1	1627[c]
	a_1		3463.9	3337[c]
	e		3592.5	3444[c]
N_2H (C_s)	a′	1098.5	1108.1	
	a′	1785.6	1802.6	
	a′	2866.5	2891.3	
N_2H ($C_{\infty v}$)[j]	π	1486.8*i*	1468.6*i*	
	π	530.5	616.7	
	σ	1937.7	1933.8	
	σ	3785.0	3802.5	
cis-N_2H_2	a_2	1231.5	1247.9	
	a_1	1351.2	1364.2	
	b_2	1535.5	1553.9	
	a_1	1554.3	1563.3	
	b_2	3108.9	3146.8	
	a_1	3196.8	3232.0	
trans-N_2H_2	a_u	1305.5	1317.5	1288.6[d]
	b_u	1334.1	1343.9	1316.4[d]
	a_g	1547.1	1551.5	1529[e]
	a_g	1604.3	1612.1	1583[e]
	a_g	3233.2	3264.8	3128[e]
	b_u	3263.3	3297.2	3120.3[d]
N_2H_3	a	606.3		
	a	708.9		
	a	1136.3		
	a	1213.4		
	a	1477.5		
	a	1646.7		
	a	3377.3		
	a	3471.9		
	a	3622.2		
$N_2H_3^+$	a″	1059.5	1056.6	
	a′	1195.1	1194.4	
	a″	1230.2	1239.0	
	a′	1491.6	1493.6	
	a′	1586.6	1593.0	
	a′	1733.2	1734.0	
	a′	3321.4	3339.9	
	a′	3337.7	3354.7	
	a′	3472.6	3473.8	
N_2H_4	a	404.1	406.0	376.7[f]
	a	841.7	840.7	780[g]
	b	1026.6	1020.0	966[h]
	a	1104.6	1114.0	1076[g]
	b	1292.7	1302.7	1275[h]
	a	1332.3	1338.7	1275[g]
	b	1651.2	1674.0	1628[h]
	a	1665.3	1685.2	1642[g]
	b	3426.0	3460.0	3314[h]
	a	3436.8	3469.0	3329[g]
	a	3535.8	3563.8	3398[g]
	b	3538.6	3569.0	3350[h]
$N_2H_5^+$ [i]	a″	326.6	335.8	
	a′	900.6	909.7	973
	a″	1045.6	1052.7	1246
	a′	1054.3	1059.2	1101
	a′	1209.8	1213.7	1124
	a″	1436.6	1448.1	1584
	a′	1531.5	1554.5	1417
	a′	1641.4	1663.9	1510
	a″	1655.4	1678.8	1638
	a′	1680.9	1699.6	1610
	a′	3355.4	3376.9	2716
	a′	3418.3	3434.1	2950
	a″	3465.1	3480.5	3034
	a′	3490.1	3506.5	3150
	a″	3519.6	3532.1	3261

[a] All frequencies calculated at the CCSD(T) level except for N_2H which were obtained at the DFT level with the B3LYP exchange-correlation functional. [b] Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure Constants of Diatomic Molecules*; Van Nostrand-Reinhold: New York, 1979. [c] Shimanouchi, T. *Tables of Molecular Vibrational Frequencies*; Consolidated Vol. 1, NSRDS NBS-39. [d] Reference 39. [e] Reference 38. [f] Reference 41. [g] Reference 40. [h] Reference 42. [i] References 37a and 44. [j] Broken symmetry solution for linear N_2H.

TABLE 3: Calculated Dissociation Energies at 0 K[a]

molecule	CBS(2)[b]	CBS(3)[c]	ΔE_{ZPE}[d]	ΔE_{CV}[e]	ΔE_{SR}[f]	$\sum D_0(2)$[g]	$\sum D_0(3)$[h]
N_2	227.15	227.48	3.36	0.63	−0.12	224.31	224.63
NH_3	297.45	297.48	21.09	0.34	−0.29	276.41	276.54
N_2H (C_s)	223.56	223.72	8.16[i]	0.67	−0.27	215.81	215.97
N_2H ($C_{\infty v}$)	196.34	196.41	8.93[i]	0.88	−0.35	187.93	188.01
cis-N_2H_2	290.12	290.28	17.03[i]	0.63	−0.34	273.37	273.53
trans-N_2H_2	295.49	295.64	17.42	0.67	−0.36	278.38	278.54
N_2H_3[j]	347.64		24.38[k]	0.98	−0.49	323.75	
$N_2H_3^+$	173.92		25.99[i]	0.81	−0.41	148.34	
N_2H_4	437.30	437.42	32.80	1.00	−0.54	404.96	405.08
$N_2H_5^+$	337.89		42.29[k]	1.06	−0.55	296.12	

[a] Results are given in kcal/mol. [b] Extrapolated by using eq 2 with aV*n*Z, where n = D, T, and Q. [c] Extrapolated by using eq 3 with aVQZ and aV5Z. [d] The zero point energies were obtained from the average of CCSD(T)/aVTZ and experimental values, when available, as reported in Table 2. See text for details. [e] Core/valence corrections were obtained with the cc-pwCVTZ basis sets at the CCSD(T)/aVTZ optimized geometries. [f] The scalar relativistic correction is based on a CISD/aVTZ calculation. [g] $\sum D_0$ computed with the CBS extrapolation obtained by using eq 2. [h] $\sum D_0$ computed with the CBS extrapolation obtained by using eq 3. [i] A scale factor of 0.983, obtained from *trans*-N_2H_2, was used. [j] For the ZPE, CCSD(T)/aVDZ values were used. [k] A scale factor of 0.987, obtained from N_2H_4, was used.

with an NH^+ substituent. Highly electropositive substituents tend to lower the inversion barrier in amines consistent with the overall planar structure. In contrast, N_2H_3 has a nonplanar structure with a pyramidalized $(HN)^+NH_2$ group and a N−N bond that is ~0.1 Å longer than the N−N bond in $N_2H_3^+$. $N_2H_5^+$ is similar to N_2H_4 with a long N−N single bond that is slightly lengthened from that in N_2H_4. The molecule can be described best as a protonated amine with a NH_2 substituent. The N−N bond distance in the ion is in reasonable agreement with the value of 1.44 Å from experiment.[37]

The calculated vibrational frequencies are given in Table 2 and compared to experiment for N_2H_2 and N_2H_4. Martin and co-workers[6,7] have done an excellent job on analyzing the results for N_2H_2 so we do not do so here, except to note that the computed harmonic values are larger than the experimental ones[38,39] as expected, especially for the N−H stretches where the effects of anharmonicity are the largest.

Durig and co-workers[40] have assigned most of the vibrational frequencies for the a symmetry modes in N_2H_4 except for the lowest a mode that was obtained by Yamaguchi et al.[41] The agreement is reasonable with the calculated harmonic values higher than the experimental ones which contain anharmonic contributions as expected. To evaluate the thermodynamic properties of N_2H_4, the frequencies of the b symmetry modes were estimated.[42] On the basis of the comparison with the a symmetry modes, it is clear that the highest energy N−H stretching mode of b symmetry has been estimated to be too low. The remaining b symmetry modes are reasonable estimates based on comparison with the calculated values.

For N_2H (nonlinear), the N−H stretch is predicted to be lower than that in N_2H_2. The N−N bond stretch is predicted to be at 1803 cm^{-1} in comparison to values for N_2 of 2340 cm^{-1} with the aVTZ basis set and an experimental harmonic value of 2360 cm^{-1}.[43] For $N_2H_3^+$, the N−N stretch at 1734 cm^{-1} is higher than the stretch at 1612 cm^{-1} (1583 cm^{-1}, experiment) calculated for *trans*-N_2H_2. The N−H stretches are predicted to be higher than those in N_2H_2 but not as high as those in N_2H_4. For N_2H_3, the N−N stretch is lower than those of *trans*-N_2H_2 and $N_2H_3^+$, 1213 cm^{-1} versus 1604 and 1733 cm^{-1}, respectively, at the CCSD(T)/aVTZ level. For $N_2H_5^+$, the calculated N−N stretch (1059 cm^{-1}) is lower than that for N_2H_4 (1114 cm^{-1}, calculated; 1076 cm^{-1}, experiment[40]).

The vibrational spectrum for $N_2H_5^+$ has been reported[44] and analyzed by a force field approach.[37a] We note that a number of assumptions were made in the symmetry assignments which are not correct so we prefer our ordering.

TABLE 4: CCSD(T) Calculated and Experimental Heats of Formation at 0 and 298 K (kcal/mol)[a]

molecule	ΔH_f(0K)[b]	ΔH_f(0K) exptl	ΔH_f^0(298K)[b]	ΔH_f^0(298K) exptl
N_2	0.6	0.0	0.6	0.0
NH_3	−9.1	−9.30 ± 0.10[c]	−10.7	−10.98 ± 0.08[e]
N_2H (C_s)	60.8		60.1	
N_2H ($C_{\infty v}$)	88.7		87.8	
cis-N_2H_2	54.9		53.2	
trans-N_2H_2	49.9	≥48.8 ± 0.5[d]	48.1	≥46.6 ± 0.8[f]
N_2H_3	56.2		53.7	
$N_2H_3^+$	231.6		228.9	
N_2H_4	26.6	26.2[c]	23.1	22.8 ± 0.2[c]
$N_2H_5^+$	187.1		182.7	

[a] Additional useful values: $\Delta H_f^0(NH) = 85.92$ kcal/mol, $\Delta H_f^0(NH_2) = 45.27$ kcal/mol, $\Delta H_f^0(NH_3) = -9.10$ kcal/mol at 0 K. $\Delta H_f^0(NH) = 85.94$ kcal/mol, $\Delta H_f^0(NH_2) = 44.58$ at 298 K. At 0 K, $\Delta H_f(H^+) = 365.22$ kcal/mol and at 298 K, $\Delta H_f^0(H^+) = 365.7$ kcal/mol. See refs 4 and 31. [b] The reported heats of formation were obtained by averaging $\sum D_0(2)$ and $\sum D_0(3)$ where available or using $\sum D_0(2)$ if that is the only available value. [c] Reference 31. [d] Reference 8. [e] Reference 45. [f] Reference 50.

The energy components used in calculating the total dissociation energy to atoms are given in Table 3 for use in eq 4. The values with the two extrapolation procedures are within 0.2 kcal/mol of each other, suggesting that the error in the extrapolation procedure is ±0.2 kcal/mol. The core valence ΔE_{CV} corrections are modest ranging from 0.63 to 1.06 kcal/mol, and the scalar relativistic ΔE_{SR} corrections are somewhat smaller and of opposite sign ranging from −0.27 to −0.55 kcal/mol.

The predicted heats of formation are given in Table 4. We have included the values for N_2 and NH_3 for comparison. The calculated heat of formation for N_2 is too positive by 0.6 kcal/mol as compared to the experimental value.[31] The calculated values for $\Delta H_f(NH_3)$ are in excellent agreement with the experimental values of 9.30 ± 0.10 kcal/mol[31] at 0 K and 10.98 ± 0.08 kcal/mol[45] at 298 K. The calculated value for N_2H_2 is in excellent agreement with the experimental lower bound[8] and the calculation of Martin and Taylor.[6] The calculated heat of formation of N_2H_4 at 0 and 298 K is in excellent agreement with the experimental value[31] at 0 K of 26.20 ± 0.2 kcal/mol and at 298 K of 22.8 ± 0.2 kcal/mol.

The N−H bond energy in N_2H_2 is 62.5 kcal/mol and in N_2H_4 it is 81.2 kcal/mol which can be compared to the respective N−H bond energies[4] in NH_3, NH_2, and NH of 106.0, 92.3, and 78.2 kcal/mol, all at 0 K. Our calculations enable us to predict the N−N bond strengths. The N−N bond strength in N_2 is 225.1

TABLE 5: Entropies at 298 K (cal/(mol·K))

molecule	*S*(298K)	molecule	*S*(298K)
N_2H (C_s)	37.47[a]	N_2	45.78[a]
cis-N_2H_2	52.21[a]	NH	41.06[a]
trans-N_2H_2	52.15[a]	NH_2	46.49[a]
N_2H_3	56.71[b]	NH_3	49.03[a]
$N_2H_3^+$	54.32[a]	CH_3NH_2	57.53[d]
N_2H_4	55.17[a]	CH_3NNH	61.83[d]
$N_2H_5^+$	57.33[a]	CH_3NNCH_3	69.82[d]
H^+	26.04[c]	$CH_3HNNHCH_3$	71.88[d]
H_2	31.13[a]		

[a] CCSD(T)/aVTZ. [b] CCSD(T)/aVDZ. [c] Experimental value, ref 31. [d] B3LYP/aVTZ.

kcal/mol (nominal triple bond).[43] The N−N bond strength in HNNH is 121.9 kcal/mol (nominal double bond) and it is 63.9 kcal/mol in H_2NNH_2 (nominal single bond).

The proton affinity of N_2H_2 is 184.9 kcal/mol in comparison to a value of 192 kcal/mol at 298 K from a low level CISD/6-31G**//6-31G** calculation.[46] The older value is in error by about 7 kcal/mol as compared to our more reliable value. This result shows that NH^+ substitution for H reduces the proton affinity[47,48] of NH_3 by about 20 kcal/mol. The calculated proton affinity of N_2H_4 is 206.1 kcal/mol in comparison to an experimental value of 203.9 kcal/mol at 298 K.[47] The ionization energy of N_2H_3 is predicted to be 7.59 eV.

Molecular entropies are given in Table 5. The theoretical energetics for some simple hydrogenation reactions are given below (using a calculated value of $\Delta H_f(H_2) = -0.1$ kcal/mol at 298 K).

$$N_2 + H_2 \rightarrow N_2H_2 \tag{8}$$

$$\Delta H(298K)\ \text{kcal/mol} = 47.6;\ \Delta G(298K) = 55.0\ \text{kcal/mol}$$

$$N_2H_2 + H_2 \rightarrow N_2H_4 \tag{1a}$$

$$\Delta H(298K) = -24.9\ \text{kcal/mol};\ \Delta G(298K) = -16.5\ \text{kcal/mol}$$

As expected, hydrogenation of N_2 (reaction 8) is an endothermic process whereas hydrogenation of N_2H_2 (reaction 1a) is an exothermic process. Hydrogenation of N_2H_4 to form two NH_3 molecules (reaction 9) is also an exothermic process and the values of the enthalpy and free energy are comparable. The experimental value of −44.8 kcal/mol for ΔH(298K) for reaction 9 is in excellent agreement with our calculated value.

$$N_2H_4 + H_2 \rightarrow 2NH_3 \tag{9}$$

$$\Delta H(298K) = -44.4\ \text{kcal/mol};\ \Delta G(298K) = -47.9\ \text{kcal/mol}$$

To estimate the heats of formation for CH_3NNH, CH_3NNCH_3, and $CH_3HNNHCH_3$, we calculated the energy of the isodesmic reactions 5−7 and used the experimental values for CH_3NH_2 (−1.9 kcal/mol at 0 K and −5.4 kcal/mol at 298 K)[49] and NH_3 (−9.30 kcal/mol at 0 K and −10.98 kcal/mol at 298 K),[31] and our computed values for N_2H_2 and N_2H_4. The results for the reaction energies are given in Table 6. The differences in the minimum and maximum values for each of reactions 5, 6, and 7 are 1.2, 2.9, and 3.9 kcal/mol, respectively. The DFT values are consistently lower than the MP2 values. There is not a large basis set dependence for either the DFT or MP2 calculations, both less than 1 kcal/mol. To calculate the heats of formation, we used the MP2/CBS values with the results given in Table 7.

We also calculated the heats of formation at the G3(MP2) level[17] as given in Table 7. We see that for all of the compounds, the G3(MP2) method gives heats of formation that are too positive for NH_3, CH_3NH_2, N_2H_2, and N_2H_4. Thus the G3(MP2) heats of formation for the methyl derivatives are too positive as compared to our isodesmic reaction values because the energetics of the underlying base structures are too positive.

Our heats of formation for the methyl derivatives allow us to predict the hydrogenation energy of the following reaction:

$$CH_3NNCH_3 + H_2 \rightarrow CH_3HNNHCH_3 \tag{1b}$$

$$\Delta H(298K) = -13.8\ \text{kcal/mol};\ \Delta G(298K) = -5.1\ \text{kcal/mol}$$

We note that the introduction of methyl groups makes the reaction substantially less exothermic demonstrating that we can design an organic reaction that will have the appropriate substituents to make the reaction more thermoneutral. This will be critical for chemical hydrogen storage systems which need to be near thermoneutral to minimize the energy needed to liberate the hydrogen and to regenerate the storage material.

Conclusion

The heats of formation of N_2H_x compounds were calculated by using ab initio molecular orbital theory at the CCSD(T)/CBS level. Our calculated results are in very good agreement with the available experimental values. These values were used to calculate ionization energies, proton affinities, bond energies, and hydrogenation energies. We calculated the heats of formation of $N_2(H)_x(CH_3)_y$ molecules by using an isodesmic reaction approach with reaction energies calculated at the MP2/CBS level. We also calculated the heats of formation of the N_2H_x and the $N_2(H)_x(CH_3)_y$ molecules at the G3(MP2) level. The G3(MP2) heats of formation for the N_2H_x molecules are higher in energy than those obtained with the CCSD(T)/CBS procedure and are not in as good agreement with the experiment. The calculated results for the hydrogenation reactions show that substitution of an organic substituent for H improves the

TABLE 6: Comparison of Calculated Enthalpies (kcal/mol) for Reactions 5, 6, and 7[a]

	ΔE(0K)			ΔH^0(298K)		
level of calculation	reaction 5	reaction 6	reaction 7	reaction 5	reaction 6	reaction 7
B3LYP/DGDZVP2	−10.99	−20.61	−8.13	−11.54	−21.94	−9.44
B3LYP/6-311++G**	−10.56	−19.97	−8.23	−11.15	−21.35	−9.58
B3LYP/aVDZ	−10.66	−20.09	−8.43	−11.30	−21.59	−9.83
B3LYP/aVTZ	−10.90	−20.64	−8.39	−11.51	−22.09	−9.79
MP2/aVDZ	−11.46	−22.33	−12.04	−12.07	−23.78	−13.44
MP2/aVTZ	−11.73	−22.84	−11.65	−12.34	−24.29	−13.05
MP2/aVQZ	−11.64	−22.67	−11.44	−12.26	−24.11	−12.84
MP2/CBS(1)[b]	−11.57	−22.53	−11.31	−12.19	−23.98	−12.71
G3(MP2)[c]	−10.83	−21.06	−11.22	−11.40	−22.41	−12.40

[a] The thermal corrections to the enthalpies at the MP2 level for calculating $\Delta H°$(298K) were taken from B3LYP/aVTZ calculations. [b] MP2/CBS(1) + ZPE (B3LYP/aVTZ) = ΔH^0(0K): −12.39 (reaction 5), −24.70 (reaction 6), −13.37 (reaction 6) kcal/mol. [c] G3(MP2) values at 0 K do not include ZPE, the corresponding values with ZPE are ΔH^0(0K): −11.63 (reaction 5), −23.19 (reaction 6), −13.09 (reaction 7) kcal/mol.

TABLE 7: G3(MP2) Heats of Formation and Heats of Formation from Isodesmic Reactions at 0 and 298 K (kcal/mol)

molecule	ΔH_f(0K) G3(MP2)	$\Delta H_f{}^0$(298K) G3(MP2)	ΔH_f(0K) isodesmic	$\Delta H_f{}^0$(298K) isodesmic
NH_3	−8.3	−10.0		
trans-N_2H_2	50.7	49.0		
N_2H_4	28.8	25.3		
CH_3NH_2	−0.5	−4.1		
CH_3NNH	46.9	43.5	44.9	41.5
CH_3NNCH_3	43.2	38.4	40.0	35.3
$CH_3HNNHCH_3$	31.3	24.7	28.0	21.5

energetics (with respect to reversibility and ease of reaction), suggesting that these types of compounds may be possible to use in a chemical hydrogen storage system.

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Supporting Information Available: Total CCSD(T) energies (E_h) as a function of basis set. This material is available free of charge via the Internet at http://pubs.acs.org.

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