Density Functional Calculations of Thermochemical Equilibria

Hansong Cheng,* Vipul S. Parekh, John W. Mitchell, and Kathryn S. Hayes

Air Products and Chemicals, Inc., 7201 Hamilton Boulevard, Allentown, Pennsylvania 18195-1501

Received: July 17, 1997; In Final Form: December 9, 1997

Computationally practical quantum-mechanical methods are needed in order to determine the ideal-gas thermodynamic properties of moderate-size molecules. In this work, we attempt to utilize density functional theory with B3LYP functional to calculate thermodynamic quantities of organic molecules of moderate sizes and to apply the results to characterize the thermochemical equilibria of industrially important amines systems. It was found that the B3LYP calculations with the 6-31G** basis set systematically underestimate the heat of combustion. A molecular-size-dependent scaling factor was then defined to systematically scale up the calculated heat of combustion, yielding good agreement with the well-established tabulated data. The heat of formation can be readily derived from the scaled heat of combustion. We show that single point energy calculations with the 6-311++G** basis set using the geometries and vibrational frequencies obtained at the 6-31G** level can greatly improve the quality of the calculated heats of formation. The calculated entropy and heat capacity are in good agreement with the tabulated values. The calculated Gibbs free energy of a molecule is also consistent with the tabulated data over a wide temperature range with the inaccuracy mainly resulting from the uncertainty of heat of formation. The calculated Gibbs free energy changes used to characterize the chemical equilibria in amine syntheses are in general within 2 kcal/mol difference from the tabulated data. The error is magnified in the calculated equilibrium constants.

Introduction

Quantitative determination of thermodynamic properties of a molecular system from quantum-mechanical first principles is a long-sought goal in computational chemistry and has been an area of intensive research recently.[1−6] Considerable effort has been devoted to applying high-level quantum-mechanical methods such as G2 theory to directly calculate thermochemistry for small molecules.[7,8] Several studies making use of isodesmic reactions have shown that high-level theoretical methods, coupled with experimental heats of formation for a few simple molecules with well-studied thermodynamic properties, are capable of yielding heats of formation for a given molecular system within ±2 kcal/mol.[2,3,5−7,9] Sophisticated quantum-mechanical calculations of equilibrium properties for an individual molecule require considerable computational resources since the second-order derivatives of the potential energy surface must be evaluated. Consequently, many high-level first-principle calculations were performed only for electronic energies, which were then used to calculate the thermochemistry of specific chemical reactions.[10,11] Although the formalism of calculating thermodynamic quantities based on quantum statistical mechanics was worked out many years ago, little progress has been made in directly calculating the equilibrium constants for given chemical reactions.

There have been many recent studies that demonstrate the value of density functional theory (DFT) in providing accurate molecular geometries, electronic energies, and vibrational frequencies at a moderate computational cost.[12−15] By explicitly taking into account the electron correlation effect, DFT methods surpass the conventional Hartree−Fock ab initio methods (HF) in providing often accurate electronic energy for a molecule.[16] Many studies have shown that the calculated results are, in general, superior to post-HF treatment.[17−20] In particular, the inclusion of HF exchange coupled with gradient-corrected correlation functional as proposed by Becke has shown great improvement in computational accuracy.[12,21] There has been very limited effort, however, in applying this method to calculate the chemical equilibria characterized by equilibrium constants. It is well-understood that the free energy change of a chemical reaction is a more sensitive quantity to computational accuracy than the reaction heat because a small difference of free energy will result in a considerable change in the equilibrium constant.

The purpose of the present paper is to utilize the hybrid HF-DFT method to explore the possibility of directly calculating the chemical equilibria for a given organic reaction, with a particular emphasis on the industrial synthesis of amine systems. Our main objective is to develop a practical scheme to quantitatively or semiquantitatively evaluate thermochemical properties for molecules of industrial interest using moderately high-level quantum-mechanical methods. The information is required for a variety of applications in experimental and process design and in kinetic analysis of a reacting system to define the compositional driving force terms.[22] Understanding the equilibria and kinetics is essential in order to develop a scheme to optimize the formation of the desirable products. Unfortunately, reliable thermodynamic data for molecules under the conditions of interest are often unavailable or incomplete. Furthermore, many of the experimental data on thermodynamic quantities are outdated, and there are also considerable discrepancies between different experimental measurements. Therefore, they often fail to serve as a reliable source for estimating reaction equilibria for experimental and process design. Experimentally, it is usually tedious to obtain the reaction equilibrium information since the measurement must be carried out at very long residence/space time with a variety of compositions and temperatures in order to correlate the equilibrium over a range of conditions. Such a measurement is particularly challenging when the molecules under investigation are chemically unstable or are reactive intermediate species. It

---

* Corresponding author (chengh@apci.com).

S1089-5639(97)02330-X CCC: $15.00

is therefore highly desirable to obtain the chemical equilibrium information from alternative sources.

In this paper, we report the results of quantum-mechanical first-principles calculations of thermodynamic properties of moderate-size organic molecules. The calculated heat capacity and entropy of individual molecules are used to evaluate the chemical equilibrium constants for several reaction processes involved in amine synthesis. The results are compared with the data obtained from values tabulated in the literature.[23,24] It is generally accepted that these tabulated data are reliable for small organic molecules, although some experimental evidence suggests that the reliability diminishes slowly as the molecular size increases since some of the data are obtained via highly empirical methods. We show in this paper that moderately high-level electronic structure calculations are potentially capable of providing quantitative or semiquantitative thermoequilibrium information for moderate-size organic systems and can be used to study chemical equilibria for reaction processes.

Computational Details

The electronic structure calculations were carried out by utilizing the adiabatic connection method, which employs a hybrid functional (B3LYP) based on a HF exchange and a gradient-corrected correlation provided by DFT.[21,25] The calculations were performed using the standard 6-31G** and 6-311++G** basis sets provided by the PS-GVB program suite.[26] Furthermore, the present methods utilize the pseudospectral techniques to speed up the computational process. All of the molecular geometries were fully optimized. Normal-mode analysis was then carried out to obtain vibrational spectra.

Ideal-gas thermodynamic quantities can be readily calculated upon determination of electronic and geometric structures and the vibrational frequencies.[27] In the present study, we are mainly interested in three fundamental quantities that determine the system equilibrium properties: heat capacity, entropy, and heat of formation. While calculations on heat capacity and entropy were readily done by using the standard procedure in quantum statistics, the heat of formation was evaluated by employing two alternative methods. The first method is to directly calculate the heat of formation using the procedure by Curtiss et al.[28] The second one is to derive the heat of formation from heat of combustion by making use of the experimental heats of formation of CO_2, H_2O, O_2, and N_2.

Results and Discussions

The optimized structures and frequencies are compared with the available experimental data. As expected, the B3LYP method with both 6-31G** and 6-311++G** basis sets yields reasonably accurate molecular structures and vibrational frequencies. In general, we found that the calculated bond lengths and angles are within 0.015 Å and 2° compared with the experimental values, respectively. The calculated vibrational frequencies are also in good agreement with the available experimental data. Since the structures and vibrational frequencies of the molecules in the present study have been extensively calculated and published in the literature and our primary focus here is on the thermodynamic quantities, we refrain from showing the fully optimized geometric parameters and frequencies (see Table in the Supporting Information).[12,13,16,29−32]

Figure 1 displays the calculated absolute entropy done at the 6-31G** level vs the tabulated data for the molecules labeled in the figure. Over the entire temperature range, the calculated entropy is in good agreement with the tabulated data. However, there are some systematic and essentially constant deviations from the tabulated values. The larger the molecule, the larger the deviation from the tabulated entropy. This may be mainly attributed to the fact that the long chains in the large molecules, such as butylamines, give rise to a variety of conformations that result in a certain degree of uncertainty in the low vibrational frequency modes. The present calculation only takes the lowest energy conformation into account. The absolute and relative deviations of the calculated entropy from the tabulated one at 300 K are shown in Table 1. There is only a slight improvement on the quality of the calculated entropy with the 6-311++G** basis set.

In Figure 2, the heat capacity C_p calculated at the 6-31G** level as a function of temperature at 1 atm for the above molecules is depicted. Again the calculated values are in excellent agreement with the tabulated data, particularly in the high-temperature regime. At low temperature, however, the calculated heat capacities deviate slightly from the tabulated values. Once again, we also observe systematic deviation of heat capacity as molecular size increases. The largest deviation was found to be less than 4 cal/mol K at the lower temperature. Table 2 shows the absolute and relative deviations of the calculated heat capacities from the tabulated ones at 300 K. The improvement using the larger basis set is only marginal, and again, the deviation increases with molecular size.

In Table 3, we list the calculated electronic energies, the zero-point energy, the vibrational energy changes from 0 K to room temperature, and the absolute enthalpies required to evaluate the heats for the molecules listed in Figure 1. Pople and co-workers proposed a scheme to scale down the calculated vibrational frequencies to match the experimental values.[33] We adopted the scaling factor recommended by Radom and co-workers for the B3LYP method to recalculate the harmonic frequencies, which are then used to calculate the heats of combustion.[32] The calculated contributions to the vibrational energies using the scaled vibrational frequencies are also shown in Table 3.

We first calculate the heats of combustion for the molecules except for H_2O, CO_2, O_2, and N_2, whose heats of formation are well-defined. The calculated heats of combustion are shown in Table 4, where the heats of combustion derived from tabulated values of heats of formation are also listed. It is seen that in general the hybrid HF-DFT method with the 6-31G** basis set systematically underestimates the heat of combustion for these molecules compared with the tabulated data. While large deviation from the tabulated values is observed in large molecules, the percentage of the deviation is molecular-size-dependent: the larger the molecule, the smaller the percentage. To reflect the size effect on the calculated heat of combustion, we propose a size-dependent scaling scheme that allows scaling the calculated heats of combustion to match the tabulated values. This scaling scheme can be described as follow: for a given organic molecule with formula $H_uC_vN_wO_x$, we consider the combustion reaction

$$H_uC_vN_wO_x + yO_2 \rightarrow (u/2)H_2O + vCO_2 + (w/2)N_2 \quad (1)$$

where $y = u/4 + v - x/2$. Then the molecular size is characterized by

$$n = w/2 + v + u/2 - y - 1 \quad (2)$$

Subsequently, we define a size-dependent scaling factor

$$f(n) = 1.128(1 + e^{-2(n+1)}) \quad (3)$$

to multiply the calculated heat of combustion. The scaled heats

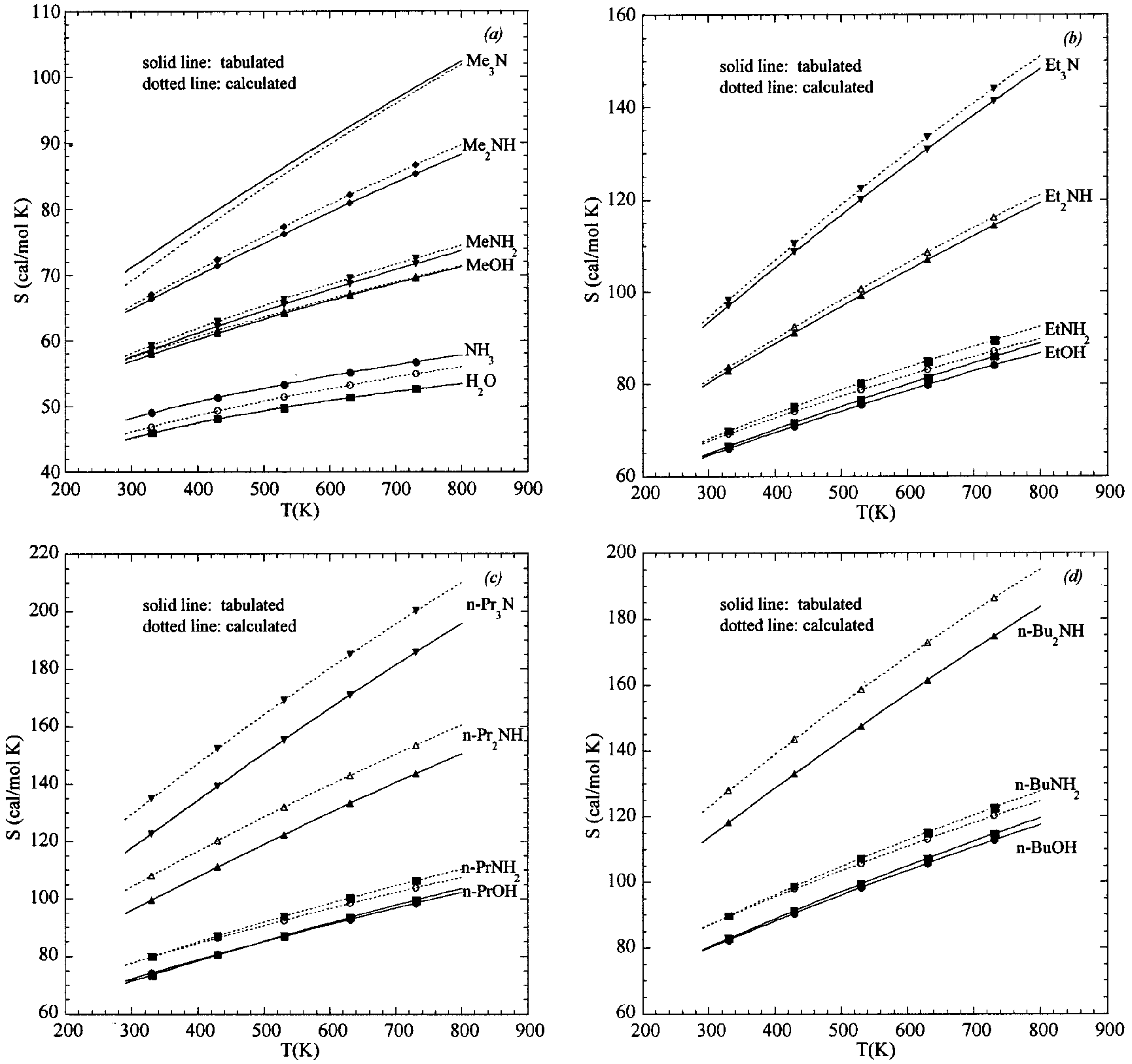

Figure 1. Calculated vs tabulated absolute entropy.

TABLE 1: Absolute and Relative Deviation of the Calculated Entropy from the Tabulated Entropy at $T = 300$ K (Units: for Absolute Deviation, cal/mol·K; for Relative Deviation, Percentage)

	absolute deviation		relative deviation	
molecule	6-31G**	6-311++G**	6-31G**	6-311++G**
H_2O	0.024	−0.01	0.05	0.0
MeOH	−0.54	−0.22	−0.95	−0.38
EtOH	−3.13	−2.95	−4.85	−4.55
PrOH	−5.50	−5.02	−7.61	−6.90
BuOH	−7.05	−6.57	−8.83	−8.18
NH_3	2.13	2.14	4.43	4.43
$MeNH_2$	−0.57	−0.41	−0.99	−0.71
Me_2NH	−0.55	−0.42	−0.86	−0.65
Me_3N	1.97	1.80	2.77	2.54
$EtNH_2$	−3.24	−3.10	−4.99	−4.76
Et_2NH	−0.68	−1.77	−0.85	−2.23
Et_3N	−1.10	0.24	−1.17	0.25
$PrNH_2$	−6.16	−6.16	−8.62	−8.62
Pr_2NH	−8.31	−6.09	−8.66	−6.20
Pr_3N	−11.79		−10.01	
$BuNH_2$	−6.66	−5.50	−8.30	−6.75
Bu_2NH	−9.29	−8.52	−8.17	−7.44

of combustion are also shown in Table 4. It is seen that the scaled values are in good agreement with the tabulated ones.

Figure 3 displays the ratio of the tabulated heats of combustion over the calculated values for the molecules listed in Table 1. The size-dependent scaling factor is also shown in the figure. It is seen that the scaling factor defined by eq 3 represents the error percentage reasonably well. It is possible, however, that the scaling factor can be further refined if one takes into account specific groups of organic molecules.

Taking into account the tabulated values of heats of formation for CO_2, H_2O, O_2 and N_2, we obtain the heat of formation for the molecule $H_uC_vN_wO_x$ from the scaled heat of combustion

$$\Delta H_{\mathrm{f}}^{298} = -57.837 \times \frac{u}{2} - 94.054 \times v - \Delta H_{\mathrm{com}}^{298} \qquad (4)$$

where $\Delta H_{\mathrm{com}}^{298}$ is the heat of combustion. The calculated heats of formation and the tabulated values are shown in Table 5. It is seen that the calculated heats of formation are in reasonable agreement with the tabulated values although considerable differences between some of them are still observed. It is important to notice that while the relative difference between the calculated and tabulated heats of combustion is negligible in view of the large values of heats of combustion, the error in the calculation is exactly transferred to the calculated heats of

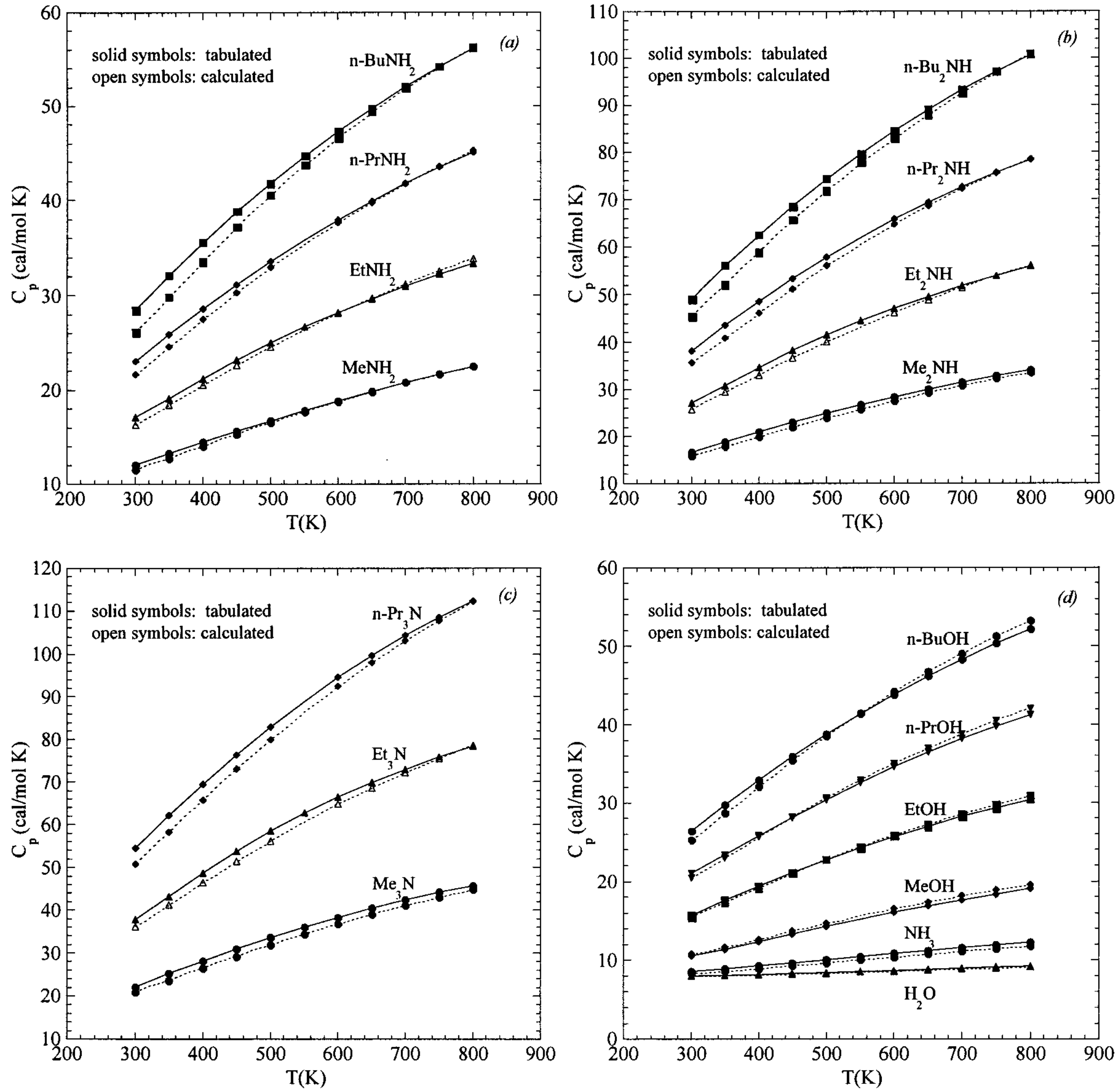

Figure 2. Calculated vs tabulated heat capacity.

TABLE 2: Absolute and Relative Deviation of the Calculated Heat Capacity from the Tabulated Heat Capacity at *T* = 300 K (Units: for Absolute Deviation, cal/mol·K; for Relative Deviation, Percentage)

	absolute deviation		relative deviation	
molecule	6-31G**	6-311++G**	6-31G**	6-311++G**
H_2O	−0.01	0.02	−0.16	0.22
MeOH	−0.20	−0.39	−1.88	−3.56
EtOH	−0.16	−0.07	−1.06	−0.43
PrOH	−0.59	−0.42	−2.91	−2.02
BuOH	−1.11	−0.95	−4.40	−3.74
NH_3	−0.22	−0.13	−2.65	−1.52
$MeNH_2$	−0.51	−0.36	−4.49	−3.06
Me_2NH	−0.76	−0.63	−4.77	−3.97
Me_3N	−1.28	−1.26	−6.15	−6.02
$EtNH_2$	−0.85	−0.66	−5.21	−4.03
Et_2NH	−1.30	−1.12	−5.04	−4.31
Et_3N	−1.69	−1.60	−4.69	−4.43
$PrNH_2$	−1.35	−1.20	−6.25	−5.50
Pr_2NH	−2.44	−2.14	−6.85	−5.95
Pr_3N	−3.71		−7.30	
$BuNH_2$	−2.32	−2.11	−8.86	−7.99
Bu_2NH	−3.74	−3.61	−8.22	−7.91

formation. Therefore, the relatively small values of heats of formation make the error in the calculated heats of formation substantial.

We also used the approach outlined in a recent work by Curtiss et al. to directly evaluate the heats of formation using both 6-31G** and 6-311++G** basis sets. The calculated results are also shown in Table 5. It is seen that the heats of formation calculated at the 6-31G** level deviate significantly from the tabulated ones. The results calculated with the 6-311++G** basis set are in much better agreement with the tabulated values. The optimized molecular geometries and vibrational frequencies obtained at the 6-311++G** level are very close to those calculated at the 6-31G** level. Indeed, using the structures and frequencies obtained with the 6-31G** basis set, we calculated the atomization energies with the 6-311++G** basis set and found that the calculated heats of formation are in excellent agreement with the data calculated entirely at the 6-311++G** level with a considerable saving of computational time. One observes from Table 5 that the heats of formation derived from the heats of combustion are in general slightly closer to the tabulated values than those directly calculated. We suspect that the tabulated values of some of the larger amines have a relatively larger uncertainty for reasons to be made clear later. In Figure 4, the Gibbs free energies of the molecules are depicted. The calculated values were obtained by Curtiss' procedure with the 6-311++G**//6-31G** basis

TABLE 3: Electronic Energy (E_e, au), Zero-Point Energy (E_v^0, kcal/mol), Vibrational Energy (ΔE_v^{298}, kcal/mol), Absolute Enthalpy at Room Temperature (H(298.15), kcal/mol), and Scaled Vibrational Energy (ΔE_v^{298}(0.891), kcal/mol)[a]

molecule	E_e	E_v^0	ΔE_v^{298}	H(298.15)	ΔE_v^{298} (0.89)
H_2O	−76.419	13.41	0.00	2.37	0.00
H_2	−1.178	6.40	0.0	2.07	0.0
O_2	−150.316	2.38	0.00	1.93	0.00
CO_2	−188.581	7.27	0.184	2.20	0.24
CH_4	−40.524	28.22	0.02	2.38	0.04
N_2	−109.524	3.51	0.0	5.58	0.0
MeOH	−115.723	32.27	0.29	2.66	0.36
EtOH	−155.046	50.29	0.91	3.28	1.08
PrOH	−194.362	68.22	1.70	4.08	1.95
BuOH	−233.679	86.15	2.52	4.89	2.84
NH_3	−56.557	21.63	0.02	2.39	0.03
$MeNH_2$	−95.863	40.25	0.37	2.74	0.46
Me_2NH	−135.174	5.15	0.96	3.33	1.14
Me_3N	−174.486	75.62	1.65	4.02	1.92
$EtNH_2$	−135.184	58.32	0.97	3.34	1.16
Et_2NH	−213.812	93.87	2.57	4.95	2.91
Et_3N	−292.436	129.14	4.26	6.63	4.77
$PrNH_2$	−174.503	75.96	1.69	4.06	1.98
Pr_2NH	−292.445	129.47	4.26	6.63	4.75
Pr_3N	−410.395	182.72	6.81	9.05	7.55
$BuNH_2$	−213.817	94.15	2.58	4.95	2.93
Bu_2NH	−371.078	165.19	6.07	8.44	6.70

[a] The calculation was done at the 6-31G** level.

TABLE 4: Calculated, Tabulated, and Scaled Heats of Combustion (Units: kcal/mol)

molecule	ΔH_{com}^{298} (calcd)	ΔH_{com}^{298} (tabd)[a]	ΔH_{com}^{298} (scaled)
MeOH	−140.02	−161.34	−165.66
EtOH	−268.42	−305.15	−308.05
PrOH	−400.42	−452.11	−454.32
BuOH	−532.52	−599.03	−601.64
NH_3	−61.59	−75.67	−75.11
$MeNH_2$	−200.46	−232.88	−232.74
Me_2NH	−336.08	−385.69	−382.96
Me_3N	−469.69	−536.19	−531.50
$EtNH_2$	−330.02	−378.76	−376.07
Et_2NH	−596.24	−676.24	−672.97
Et_3N	−865.72	−974.90	−975.86
$PrNH_2$	−459.77	−525.08	−520.28
Pr_2NH	−860.18	−969.36	−969.62
Pr_3N	−1255.56	−1413.82	−1415.03
$BuNH_2$	−593.96	−671.61	−670.40
Bu_2NH	−1124.43	−1263.14	−1267.27

[a] Derived from tabulated heats of formation.

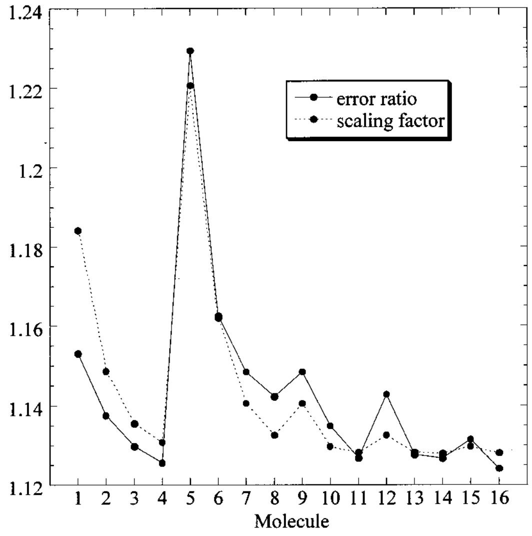

Figure 3. Ratio of the tabulated heats of combustion over the calculated values (solid line) and the size-dependent scaling factor (dashed line).

TABLE 5: Heats of Formation (Units: kcal/mol)

molecule	ΔH_f[a]	ΔH_f[b]	ΔH_f[c]	ΔH_f[d]	ΔH_f[e]
H_2O		−53.3	−57.13	−57.05	−57.84
O_2		−5.1	−0.19	−0.08	0.0
CO_2		−94.36	−92.35	−92.23	−94.05
N_2		3.26	1.08	1.27	0.0
MeOH	−44.07	−53.04	−49.15	−48.94	−48.15
EtOH	−53.57	−64.42	−56.17	−55.83	−56.08
PrOH	−59.19	−72.13	−59.53	−59.07	−60.86
BuOH	−63.76	−79.74	−62.85	−62.50	−65.68
NH_3	−11.65	−12.86	−15.04	−14.91	−10.96
$MeNH_2$	−5.90	−13.78	−9.96	−9.68	−5.49
Me_2NH	−7.57	−17.87	−8.27	−7.82	−4.42
Me_3N	−10.92	−23.33	−8.51	−8.02	−5.66
$EtNH_2$	−14.47	−23.95	−15.24	−14.87	−11.35
Et_2NH	−21.35	−37.12	−19.13	−17.75	−17.37
Et_3N	−22.24	−47.01	−18.55	−18.25	−22.16
$PrNH_2$	−22.15	−33.88	−21.31	−20.84	−16.77
Pr_2NH	−28.48	−51.34	−23.64	−23.41	−27.71
Pr_3N	−38.74	−70.01		−27.82	−38.45
$BuNH_2$	−23.92	−39.43	−21.82	−21.56	−21.97
Bu_2NH	−34.62	−67.74	−31.83	−30.42	−37.40

[a] Derived from the heats of combustion. [b] Calculated at 6-31G** level. [c] Calculated at 6-311++G** level. [d] Calculated at 6-311++G**//6-31G** level. [e] Tabulated.

set. Compared with the tabulated values, the calculated free energies are in reasonable agreement with the tabulated values, especially for smaller molecules. Consistent with the heat capacity profiles shown in Figure 2, the calculated free energy profiles show the same temperature dependence as those from tabulated values. The main difference between the calculated free energies and the tabulated data arises from the uncertainty in the heats of formation.

The primary purpose of the present study is to attempt to use first-principles methods to calculate equilibrium properties for chemical reactions of interest. As an example, we consider the industrial synthesis of amines. Industrial preparation of amines is via the exothermic reaction of alcohol and ammonia over a solid acid catalyst, typically carried out at 350−400 °C.[33]

$$ROH + NH_3 = RNH_2 + H_2O \tag{5}$$

In the present work, we are mainly interested in the synthesis

$$2RNH_2 = R_2NH + NH_3 \tag{6}$$

$$2R_2NH = R_3N + RNH_2 \tag{7}$$

of low molecular weight amines. We first examine the heats of reaction at room temperature. In Table 6, we compare the calculated heats of reaction with those derived from tabulated heats of formation. It is seen that although the heats of formation derived from the scaled heats of combustion are slightly closer to the tabulated values, the heats of reaction obtained from the directly calculated heats of formation by Curtiss' procedure are in much better agreement with the tabulated data. This is mainly due to error cancellation in the heats of reaction. The heats of reaction derived from the heats of combustion deviate considerably from the tabulated values primarily due to the error accumulation in the calculated heats of formation for the individual molecules involved. For purpose of comparison, we also show the calculated electronic energy changes for the reactions in Table 6. As expected, they are almost quantitatively consistent with the calculated heats of reaction due to the isodesmic nature of these reactions.

The significant difference in the calculated and tabulated heats of reaction for dipropylamine seems to suggest that the tabulated

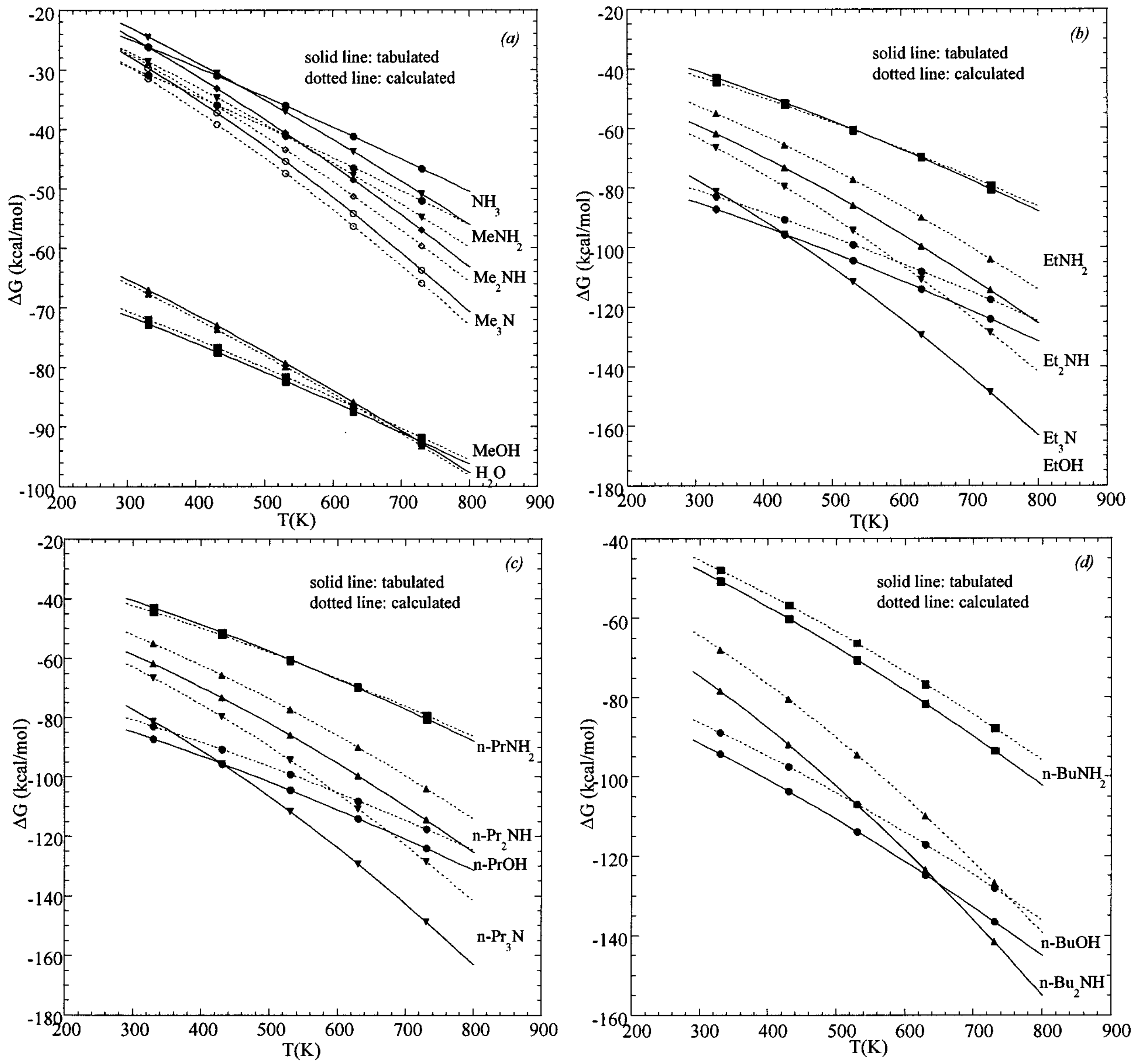

Figure 4. Calculated vs tabulated free energy.

TABLE 6: Calculated Heats of Reaction vs Tabulated Values (kcal/mol)

reaction	ΔH^a	ΔH^b	ΔH^c	ΔH^d	ΔH^e	ΔE^f	ΔE^g	ΔE^h
$MeOH + NH_3 = MeNH_2 + H_2O$	−8.03	−1.18	−2.9	−2.88	−4.22	−1.03	−2.73	−2.73
$2MeNH_2 = Me_2NH + NH_3$	−7.41	−3.17	−3.39	−3.37	−4.39	−2.79	−3.04	−2.99
$2Me_2NH = Me_3N + MeNH_2$	−1.68	−1.37	−1.93	−2.06	−2.32	−1.09	−1.66	−1.78
$EtOH + NH_3 = EtNH_2 + H_2O$	−7.09	0.03	−1.16	−1.17	−2.14	0.16	−0.94	−1.05
$2EtNH_2 = Et_2NH + NH_3$	−4.05	−2.08	−3.69	−2.94	−5.61	−1.70	−2.61	−2.55
$2Et_2NH = Et_3N + EtNH_2$	5.98	3.28	4.47	2.39	1.17	3.43	3.17	2.54
$PrOH + NH_3 = PrNH_2 + H_2O$	−7.09	−2.19	−3.87	−3.91	−2.78	−1.74	−3.32	−3.48
$2PrNH_2 = Pr_2NH + NH_3$	4.16	3.56	3.94	3.36	−5.14	3.30	3.53	3.15
$2Pr_2NH = Pr_3N + PrNH_2$	−6.43	−1.21		−1.84	0.19	−0.70		−1.36
$BuOH + NH_3 = BuNH_2 + H_2O$	−6.34	−0.13	−1.06	−1.20	−3.16	0.02	−0.79	−1.05
$2BuNH_2 = Bu_2NH + NH_3$	1.58	−1.74	−3.21	−2.21	−4.42	−1.31	−2.91	−1.77

[a] Derived from the heats of combustion. [b] Calculated at 6-31G** level. [c] Calculated at 6-311++G** level. [d] Calculated at 6-311++G**//6-31G** level. [e] Tabulated (derived from tabulated heats of formation). [f] Calculated at 6-31G** level. [g] Calculated at 6-311++G** level. [h] Calculated at 6-311++G**//6-31G** level.

heat of formation of this molecule has a large uncertainty. This suspicion is supported not only by the fact that calculations with various methods all suggest an endothermic reaction in contrast to an exothermic reaction, as suggested by the tabulated data, but also by the calculated electronic energy change, which is consistent with the calculated heat of reaction as it should be for an isodesmic reaction.

The calculated equilibrium constants for amine syntheses using the Curtiss' procedure with the 6-311++G**//6-31G** basis sets are shown as a function of temperature in Figure 5. In most of the cases, the calculated Gibbs free energies are roughly within 2 kcal/mol of the tabulated values for these reactions. Such errors are further magnified when the calculated free energies are utilized to calculate the equilibrium constants.

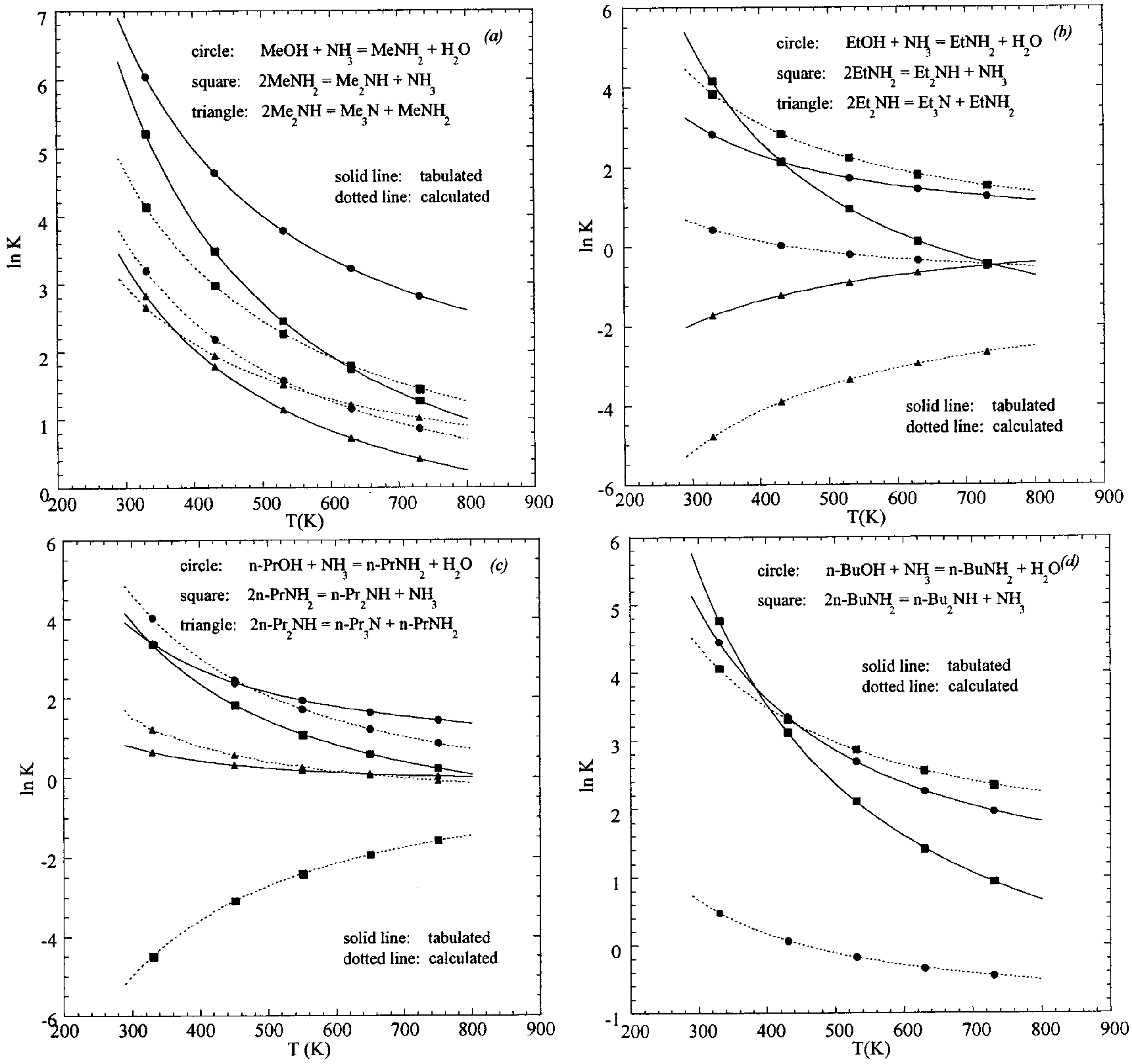

Figure 5. Calculated (dotted line) vs tabulated (solid line) equilibrium constants for reactions in amine synthesis.

It is seen that quantitatively the differences between the calculated and the tabulated equilibrium constants are considerable, although in general the calculated values preserve the same trends as the tabulated data over the temperature range. While the calculated Gibbs free energies for individual molecules are in reasonable agreement with the tabulated ones, as shown in Figure 4, there can be addition/cancellation of errors when the calculated free energies of molecules are used to evaluate the free energies of reactions. Detailed numerical analysis suggests that the significant uncertainty in the calculated free energy of a reaction is largely due to the error in the calculated heat of reaction, similar to the situation in the calculation of molecular free energies.

Summary

In this paper, we have demonstrated the potential utilities of moderately high-level quantum-mechanical calculations in providing quantitative or semiquantitative information about ideal-gas thermodynamics for moderate-size organic molecules. We have shown that the hybrid HF-DFT method coupled with appropriate basis sets is particularly useful in carrying out practical calculations for systems of industrial interest due to its computational efficiency and accuracy. It is expected that the accuracy will be considerably improved upon further development of basis sets optimized for DFT calculations. Calculated heats of formation are very sensitive to the accuracy of the electronic energy calculations.

We found that the B3LYP method systematically underestimates the heats of combustion. We then proposed a scaling scheme based on the molecular size to consistently scale up the calculated heats of combustion. The results are in good agreement with the tabulated values with very small relative differences. The heats of formation can thus be readily derived from the scaled heats of combustion. The calculated heats of formation are also in reasonable agreement with the tabulated values. The heats of formation are also derived using Curtiss' procedure. It is found that the results calculated at the 6-31G** level in general are very poor; however, the quality of the results can be significantly improved by using the optimized geometries and frequencies obtained at the 6-31G** level and the electronic energy calculated at the 6-311++G** level. This allows evaluation of thermodynamic quantities for moderate-size molecules at a considerable saving of computational time. The calculated heats of reaction for amine syntheses are essentially in good agreement with the tabulated data. We have shown that the present method is capable of yielding reliable information on the entropy and heat capacity of a molecule. It also provides quantitative or semiquantitative results on Gibbs free energies over a wide range of temperature for individual molecules. Considerable deviation in equilibrium constants from the tabulated values are observed when applying the calculated molecular free energies to evaluate the equilibrium properties of various amine synthesis reactions. The dominant factor leading to the inaccuracy is the uncertainty in the heats of formation. It is expected that the quality of the calculated heats of formation can be improved by using better electronic structure methods. The inaccuracy inherent in the calculated free energies will be significantly magnified when utilized to calculate the equilibrium constants, as expected.

Acknowledgment. We gratefully acknowledge Drs. C. A. Valenzuela, J. B. Pfeiffer, and R. Pierantozzi for their support of this research. We also thank Drs. P. M. Mathias and G. P. Pez for many useful discussions. We wish to thank Drs. W. Glausser, J. Perry, and J. Wright of Schrödinger, Inc. for their assistance and useful discussions.

Supporting Information Available: Optimized geometries and vibrational frequencies of the molecules obtained from B3LYP/6-31G** calculations (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Scuseria, G. E. *J. Chem. Phys*., **1991**, *95*, 7426.

(2) Montgomery, J. A., Jr.; Mitchels, H. H.; Francisco, J. S. *Chem. Phys. Lett*. **1994**, *220*, 391.

(3) Schneider, W. F.; Wallington, T. J. *J. Phys. Chem*. **1994**, *98*, 7448.

(4) Trout, B. L.; Chakraborty, A. K.; Bell, A. T. *J. Phys. Chem*. **1996**, *100*, 17582.

(5) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys*. **1993**, *98*, 1293.

(6) Smith, B. J.; Smernik, R.; Radom, L. *Chem. Phys. Lett*. **1992**, *188*, 589. Nicolaides, A.; Rauk, A.; Glukhovtsev, M. N.; Radom, L. *J. Phys. Chem*. **1996**, *100*, 17460.

(7) Curtiss, L. A.; Raghavachari, K.; Trucks, G. S.; Pople, J. A. *J. Chem. Phys*. **1991**, *94*, 7221. Curtiss, L. A.; Carpenter, J. E.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys*. **1992**, *96*, 9030. Raghavachari, K.; Curtiss, L. A. In *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*; Langhoff, S. R., Ed.; Kluwer: Dordrecht, 1995; p 173.

(8) Seasholtz, M. B.; Thompson, T. B.; Rondan, N. G. *J. Phys. Chem*. **1995**, *99*, 17838. Colegrove, B. T.; Thompson, T. B. *J. Chem. Phys*. **1997**, *106*, 1480.

(9) Cheung, Y.-S.; Chen, Y.-J.; Ng, C. Y.; Chiu, See-Wing; Li, Wai-Kee. *J. Am. Chem. Soc*. **1995**, *117*, 9725.

(10) Berry, R. J.; Burgess, D. R. F., Jr.; Nyden, M. R.; Zachariah, M. R.; Melius, C. F.; Schwartz, M. *J. Phys. Chem*. **1996**, *100*, 7405.

(11) Hay, P. J. *J. Phys. Chem*. **1996**, *100*, 5.

(12) Baker, J.; Muir, M.; Andzelm, J. *J. Chem. Phys*. **1995**, *102*, 2063.

(13) Ziegler, T. *Chem. Rev*. **1991**, *91*, 651 and references therein.

(14) Barone, V.; Orlandini, L. *J. Phys. Chem*. **1994**, *98*, 13185.

(15) Johnson, B. G.; Gill, P. M. W.; Pople, J. A. *J. Chem. Phys*. **1993**, *98*, 5612.

(16) Andzelm, J.; Wimmer, E. *J. Chem. Phys*. **1992**, *96*, 1280.

(17) Delley, B. *J. Chem. Phys*. **1990**, *92*, 508.

(18) Lamming, G. J.; Termath, V.; Handy, N. C. *J. Chem. Phys*. **1993**, *99*, 8765.

(19) Fitzgerald, G.; Andzelm, J. *J. Phys. Chem*. **1991**, *95*, 10531.

(20) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem*. **1992**, *70*, 560.

(21) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 1372.

(22) Mitchell, J. W.; Hayes, K. S.; Lutz, E. G. *Ind. Eng. Chem. Res*. **1994**, *33* (2), 181.

(23) Pedley, J. B.; Rylance, J. *Sussex−N.P.L Computer Analysed Thermochemical Data: Organic and Organometallic Compounds*; University of Sussex, 1977.

(24) DIPPR Project 801: *Data Compilation of Physical and Thermodynamic Properties of Pure Compounds*; AIChE: New York, **1991**.

(25) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B*. **1988**, *37*, 785.

(26) Ringnalda, M. N.; Langlois, J.-M.; Murphy, R. B.; Greeley, B. H.; Cortis, C.; Russo, T. V.; Marten, B.; Donnelly, R. E., Jr.; Pollard, W. T.; Cao, Y.; Muller, R. P.; Mainz, D. T.; Wright, J. R.; Miller, G. H.; Goddard, W. A., III; Friesner, R. A. *PS-GVB* v2.3, Schrödinger, Inc.: Portland, OR, 1996.

(27) Herzberg, G. *Molecular Spectra and Molecular Structure*; D. Van Nostrand: New York, **1966**.

(28) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys*. **1997**, *106*, 1063.

(29) Sosa, C.; Andzelm, J.; Elkin, B. E.; Wimmer, E.; Dobbs, K. D.; Dixon, D. A. *J. Phys. Chem*. **1992**, *96*, 6630.

(30) Papai, I.; St-Amant, A.; Fournier, R.; Salahub, D. R. *Int. J. Quantum Chem*. **1989**, S23.

(31) Dyer, J. R. *Applications of Absorption Spectroscopy of Organic Compounds*; Prentice-Hall, Englewood Cliffs: NJ, 1965.

(32) Scott, A. P.; Radom, L. *J. Phys. Chem*. **1996**, *100*, 16502.

(33) Pople, J. A.; Raghavachari, K.; Schlegel, H. B.; DeFrees, D.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. F.; Hehre, W. J. *Int. J. Quantum Chem., Quantum Chem. Symp*. **1981**, *15*, 269.

(34) van Gysel, A. B.; Musin, W. Methylamines. In *Ullmann's Encyclopedia of Industrial Chemistry,* 5th ed.; VCH Publishers: Deerfield Beach, FL, **1988**; Vol. A16, p 535.