Accurate Thermochemical Properties for Energetic Materials Applications. I. Heats of Formation of Nitrogen-Containing Heterocycles and Energetic Precursor Molecules from Electronic Structure Theory

Keith E. Gutowski, Robin D. Rogers,* and David A. Dixon*

Department of Chemistry and Center for Green Manufacturing, The University of Alabama, Box 870336, Tuscaloosa, Alabama 35487-0336

Received: July 11, 2006; In Final Form: August 18, 2006

The heats of formation of 1H-imidazole, 1H-1,2,4-trizazole, 1H-tetrazole, CH_3NO_2, CH_3N_3, CH_3NH_2, CH_2CHNO_2, $HClO_4$, and phenol, as well as cations and anions derived from some of the molecules have been calculated using ab initio molecular orbital theory. These molecules are important as models for compounds used for energetic materials synthesis. The predicted heats of formation of the heterocycle-based compounds are in excellent agreement with available experimental values and those derived from proton affinities and deprotonation enthalpies to <1 kcal/mol. The predicted value for the tetrazolium cation differs substantially from the experimental value, likely due to uncertainty in the measurement. The heats of formation of the nitro and amino molecules, as well as phenol/phenolate, also are in good agreement with the experimental values (<1.5 kcal/mol). The heat of formation of CH_3N_3 is predicted to be 72.8 kcal/mol at 298 K with an estimated error bar of ±1 kcal/mol on the basis of the agreement between the calculated and experimental values for $\Delta H_f(HN_3)$. The heat of formation at 298 K of $HClO_4$ is −0.4 kcal/mol, in very good agreement with the experimental value, as well as a W2 literature study. An extrapolation of the CCSD(T)/aug-cc-pV(Q,5) energies was required to obtain this agreement. This result suggests that very large basis sets (≥aug-cc-pV5Z) may be needed to fully recover the valence correlation energy contribution in compounds containing elements with high formal oxidation states at the central atom. In addition tight *d* functions are needed for the geometry predictions. Douglas−Kroll−Hess (DKH) scalar relativistic corrections for $HClO_4$ and ClO_4^- at the MP2 level with correlation-consistent DKH basis sets were predicted to be large, likely due to the high formal oxidation state at the Cl.

Introduction

High material performance has been of prime importance in the development and study of new energetic materials for various applications. However, an emerging trend in the energetic materials field has been the development of compounds with a combination of properties, including stability, high performance, reliability, safety, and low toxicity.[1] Ionic liquids (ILs) have been suggested as a potential framework for new energetic materials as they inherently incorporate many of these desirable properties.[2] ILs are low melting organic-based salts that have been developed as a class of alternative solvents for a variety of applications due to the ease with which they can be chemically manipulated to obtain a desired set of properties.[3] As a potential class of energetic materials, ILs offer high thermal stability, enhanced safety as they tend to be nonvolatile in nature (although they may be combustible[4]), and lower melting points, thus avoiding handling issues that accompany solid materials. In addition, they add intrinsic performance benefits since ILs typically possess higher densities than molecular compounds due to Coulombic interactions, which tend to favor more ordered structures both in the solid and liquid phases (ion pairing).[2,5]

Many ILs have been synthesized using nitrogen-containing heterocycles, including imidazole, 1,2,4-triazole, and tetrazole, and, as such, are a natural framework for energetic materials, as they have inherently high nitrogen contents. The hydrogens on the parent ring systems can be readily substituted with a variety of functional groups using routine chemical procedures, thus making the number of structural variations for an IL backbone nearly limitless.[6] Subsitution of the rings with energetic groups such as nitro, amino, and azido has been suggested as a way to generate energetic precursors for ILs with enhanced energetic properties due to the presence of these substituents. For example, the introduction of amino groups is one of the simplest means to enhance the thermal stability of an energetic material.[1] Adding these functionalities to the ring typically alters the heat of formation making them more positive, which is a desired characteristic for most energetic materials. Subsequently, these heterocycles may be quaternized and paired with energetic anions such as nitrate, picrate, or perchlorate to prepare new energetic materials while at the same time improving oxygen balance.[7] However, substituting the heterocycle with electron-withdrawing groups such as nitro may result in decreased susceptibility to quaternization, due to decreased ring basicity.[8] Pairing of cations with the anionic counterparts of the heterocycles, such as imidazolates, triazolates, and tetrazolates, is another potential synthetic route to generate energetic materials that has been studied.[9]

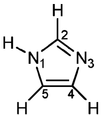
In this work, we present the first part in a study focused on the investigation of the thermodynamics characteristics of energetic salts on the basis of electronic structure calculations.

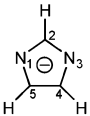
---

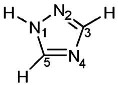
* To whom correspondence should be addressed. E-mail: rdrogers@bama.ua.edu (R.D.R.); dadixon@bama.ua.edu (D.A.D.).

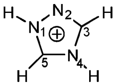
10.1021/jp0643698 CCC: $33.50

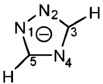
We have recently shown that electronic structure methods can successfully be used to study the formation and stability of energetic salts and ILs.[8] For such calculations, we need high-quality gas-phase heats of formation ($\Delta H_f°$), which we can obtain from ab initio electronic structure theory. This paper describes the prediction of reliable thermodynamic values of a series of small molecules and ions (**1**−**17**) that can be used as a foundation to later construct larger molecules with energetic substitutents.

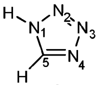

1

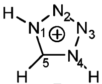

2

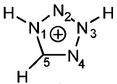

3

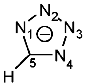

4

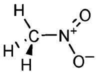

5

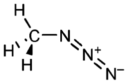

6

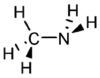

7

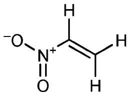

8

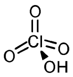

9

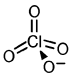

10

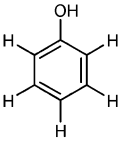

11

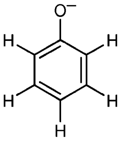

12


13


14


15


16


17

We can use isodesmic reactions to calculate the heats of formation of larger molecules as the current approach based on CCSD(T)/CBS (complete basis set) extrapolations is currently computationally intractable. An empirical modeling approach is then used to predict the lattice energies[10] and enthalpies of energetic salts and ultimately estimate the heats of formation of these materials in the solid state. This information is very important in the assessment of experimental data[11] for existing materials as well as for the design of new, potentially useful materials.[12,13]

We have been associated with a group that has been developing an approach[14] to reliably calculate the thermodynamic properties of molecules, in particular heats of formation, based on ab initio molecular orbital theory. Our approach in this work is based on this methodology for calculating the total atomization energy of a molecule and using this with well-known heats of formation of the constituent atoms to calculate the heats of formation at 0 K. This approach starts with coupled cluster theory, including a perturbative triples correction (CCSD(T)),[15] combined with correlation consistent basis sets[16] extrapolated to the CBS limit to treat the correlation energy of the valence electrons. This is followed by a number of smaller additive corrections including core-valence interactions and relativistic effects, both scalar and spin−orbit. Finally, one must include the zero-point energy obtained from theory, experiment, or some combination. The standard heats of formation of compounds at 298 K can then be calculated by using standard thermodynamic and statistical mechanics expressions.[17] This approach has been used previously to calculate the heats of formation of a range of compounds including "Arguendo-type" carbenes and adducts containing the imidazole heterocycle,[18] as well as many small H_xNO_y molecules that may play important roles as oxidizing species in various energetic processes.[19,20]

Computational Approach

For the current study, we used both the correlation consistent (cc-pV*n*Z)[16,21] and augmented correlation consistent (aug-cc-pV*n*Z)[22] basis sets for H, C, N, and O (n = D, T, Q). Aug-cc-pV(n+d)Z basis sets, containing tight *d* functions, were used for Cl atoms[23] in all calculations and will hereafter be referred to only as aug-cc-pV*n*Z. It has recently been shown that tight *d* functions are necessary for calculating accurate atomization energies for the second-row elements.[24,25] Only the spherical components (5d, 7f, 9g, and 11h) of the Cartesian basis functions were used. All of the current work was performed with the MOLPRO suite of programs,[26] NWChem suite of programs,[27] and Gaussian suite of programs.[28] All of the calculations were done on a massively parallel HP Linux cluster with 1970 Itanium-2 processors in the Molecular Sciences Computing Facility in the William R. Wiley Environmental Molecular Sciences Library or on the 144 processor Cray XD-1 computer system at the Alabama Supercomputer Center in Huntsville, AL.

The geometries of the cations (**4**, **7**, **8**) were optimized, and vibrational frequencies were calculated at the frozen core MP2 level[29] with the cc-pVTZ correlation-consistent basis set. The geometries of the neutrals (**1**, **3**, **6**, **10**, **11**, **13**, **14**, **16**) and anions (**2**, **5**, **9**, **15**, **17**) were optimized, and vibrational frequencies were calculated at the frozen core MP2 level with the aug-cc-pVTZ basis sets. The MP2-optimized geometries were used in single-point CCSD(T)/aug-cc-pVnZ (n = D, T, Q) calculations of the valence correlation energy. The open-shell CCSD(T) calculations for the atoms 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.[30−32] The orbitals were not symmetry equivalent in the atomic calculations. The CCSD(T) total energies were extrapolated to the CBS limit by using a mixed exponential/Gaussian function of the form in eq 1

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

with n = 2 (DZ), 3 (TZ), and 4 (QZ), as first proposed by Peterson et al.[33] This extrapolation procedure has been shown to yield atomization energies in the closest agreement with experiment by a small measure as compared to other extrapolation approaches up through $n = 4$. The CCSD(T)/CBS valence energy and other corrections (described below) used for calculating the atomization energy of CH_3NH_2 (**12**) were taken from Feller and Dixon[34] for the heat of formation calculation. Single-point CCSD(T) calculations using aug-cc-pV5Z basis sets were also run for CH_3NO_2 (**10**), $HClO_4$ (**14**), and ClO_4^- (**15**), and the energies (n = Q, 5) were extrapolated to the CBS limit using an expression (eq 2) suggested by Helgaker and co-workers[35]

$$E(n) = E_{CBS} + B/(l\max)^3 \quad (2)$$

Equation 2 works well if aug-cc-pV5Z basis set (or higher) energies are available. Although eq 2 was originally proposed for describing only the correlation component of the energy, we have used it to fit the total CCSD(T) energy because the Hartree−Fock component of the CCSD(T) energy is very nearly converged for such large basis sets.

Core-valence corrections, ΔE_{CV}, were obtained at the CCSD(T)/cc-pwCVTZ level of theory.[36] Scalar relativistic corrections, ΔE_{SR}, which account for the changes in the relativistic contributions to the total energies of the molecule and constituent atoms, were included at the MP2 level with the cc-pVTZ DK basis set and the spin-free, one-electron Douglas−Kroll−Hess (DKH) Hamiltonian.[37−39] Most electronic structure computer codes do not correctly describe the lowest-energy spin multiplet of an atomic state. Instead, the energy is a weighted average of the available multiplets. For N in the ^4S state, no such correction is needed, but corrections are needed for the ^3P state of C (0.08 kcal mol^{-1}), ^3P state of O (0.22 kcal mol^{-1}), and ^2P state of Cl (0.84 kcal mol^{-1}), taken from the excitation energies of Moore.[40]

The calculated MP2/aug-cc-pVTZ (cc-pVTZ for cations) vibrational frequencies of **1**−**17** were scaled to obtain zero-point energies (ZPEs). The calculated vibrational frequencies of **1**−**11** and **13**−**17** are provided in Supporting Information. The vibrational frequencies of molecules **1**−**9** were adjusted based on a scale developed for methanimine.[18] The CH stretches and bends and the NO stretches of CH_3NO_2 (**10**) were averaged with the experimental fundamentals, and the remaining frequencies were unscaled due to uncertainties in the experimental assignments.[41] The entire set of vibrational frequencies of CH_3N_3 (**11**) was averaged with the experimental fundamentals.[42] The calculated symmetric and asymmetric NO stretches of CH_2CHNO_2 (**13**) were scaled to CH_3NO_2 as determined above (scale factor = 0.972). The CC and CH stretches of **13** were adjusted by 0.984 and 0.973, respectively, based on scale factors derived from C_2H_4 (experimental values in Supporting Information).[43] The OH and ClO stretches of $HClO_4$ (**14**) were averaged with the experimental fundamentals, and the remaining frequencies were left unscaled due to good agreement with the experimental values.[44] The ClO stretches of ClO_4^- (**15**) were adjusted using a scaled factor (0.980) derived from $HClO_4$, and the remaining frequencies were unscaled. The entire set of vibrational frequencies of C_6H_5OH (**16**) was averaged with the experimental fundamentals.[45] The CH stretches and the vibrations above 1000 cm^{-1} of the phenolate anion (**17**) were separately adjusted based on scaling factors derived from (**16**) of 0.977 and 0.988, respectively. The remaining vibrations below 1000 cm^{-1} were left unscaled.

By combining our computed ΣD_0 values with the known heats of formation at 0 K for the elements ($\Delta H_f°(H) = 51.63 \pm 0.001$ kcal mol^{-1}, $\Delta H_f°(C) = 169.98 \pm 0.1$ kcal mol^{-1}, $\Delta H_f°(N) = 112.53 \pm 0.02$ kcal mol^{-1}, $\Delta H_f°(O) = 58.99 \pm 0.02$ kcal mol^{-1}, and $\Delta H_f°(Cl) = 28.59 \pm 0.001$ kcal mol^{-1}),[46] we can derive the $\Delta H_f°$ values at 0 K for molecules **1**−**17** in the gas phase. We obtain heats of formation at 298 K by following the procedures outlined by Curtiss et al.[17]

Results and Discussion

The calculated geometries of molecules **1**, **3**, **10**, **11**, **13**, **14**, and **16** are given in Tables 1−3 and compared to the experimental gas-phase structures determined from both microwave spectroscopy and gas-phase electron diffraction. The calculated structures for the remaining molecules and ions are provided in Supporting Information as no experimental data are available. The structure details of the heterocycles imidazole (**1**) and 1,2,4-triazole (**3**) are given in Table 1. The calculated MP2/aug-cc-pVTZ structure (C_s) for imidazole is in excellent agreement with the microwave structure.[47] The largest difference in the parameters is 0.013 Å for the C4−C5 bond distance and 0.8° for the C5−N1−C2 bond angle.

TABLE 1: Calculated (MP2/aug-cc-pVTZ) and Experimental Geometry[a] for 1H-Imidazole and 1H-1,2,4-Triazole

molecule	parameter	calcd	exptl[b]	exptl[c]
1	N1−C2	1.362	1.364	
	N1−C5	1.372	1.377	
	N3−C2	1.322	1.314	
	N3−C4	1.373	1.382	
	C4−C5	1.377	1.364	
	N1−H	1.006	0.998	
	C−H (avg)	1.076	1.079	
	N1−C2−N3	111.4	112.0	
	C2−N3−C4	105.2	104.9	
	N3−C4−C5	110.7	110.7	
	C4−C5−N1	105.0	105.5	
	C5−N1−C2	107.7	106.9	
	H−N1−C2	126.2	126.2	
	H−N1−C5	126.2	126.9	
	H−C2−N1	122.5	122.5	
	H−C2−N3	126.1	125.5	
	H−C4−N3	121.5	121.4	
	H−C4−C5	127.7	127.9	
	H−C5−N1	122.3	121.9	
	H−C5−C4	132.7	132.6	
3	N1−N2	1.344	1.381	1.380
	N1−C5	1.349	1.375	1.377
	N2−C3	1.336	1.328	1.329
	N4−C3	1.358	1.354	1.348
	N4−C5	1.326	1.280	1.305
	N1−H	1.007	0.998	0.990
	C−H (avg)	1.076	1.078	1.054
	N1−N2−C3	101.6	102.7	102.7
	N2−C3−N4	115.2	113.0	113.8
	C3−N4−C5	102.7	106.8	105.7
	N4−C5−N1	109.5	109.0	108.7
	C5−N1−N2	111.0	108.5	108.9
	H−N1−N2	119.7	127.5	110.9
	H−N1−C5	129.3	124.0	140.2
	H−C3−N2	121.4	128.5	127.0
	H−C3−N4	123.5	118.5	119.2
	H−C5−N1	123.5	130.5	131.0
	H−C5−N4	127.0	120.5	120.3

[a] Bond distances are in angstroms, and bond angles are in degrees. [b] From microwave spectroscopy: **1**, ref 47; **3**, ref 48. [c] From gas-phase electron diffraction: ref 49.

Both a microwave structure[48] and a gas-phase electron diffraction[49] structure for 1,2,4-triazole have been obtained, and both are compared to the calculated structure (C_s) in Table 1. The calculated structure for **3** does not agree as well with experiment as found for **1**, probably due to difficulties in experimental data refinement. The microwave and electron diffraction structures are comparable, although the calculated results are in slightly better agreement with the microwave structure. The maximum parameter differences between the calculated and microwave structures are 0.046 Å for the N4−C5 bond distance and 4.1° for the internal ring C3−N4−C5 angle. The external angles involving hydrogen atoms show much larger angle differences. Experimental data for the structure of tetrazole (**6**) is unavailable possibly due to the existence of 1-H and 2-H tautomers in the gas phase,[50] although a microwave spectrum has been collected.[51]

The calculated structures of the nitro- and azide-containing molecules (**10**, **11**, **13**) are shown in Table 2. The calculated MP2/aug-cc-pVTZ structure of molecule **10**, CH_3NO_2, is in excellent agreement with the experimental microwave structure,[52] with a maximum difference of 0.006 Å and 0.6° in the N−O and O−N−O bond distance and angle, respectively. The torsion of the CH_3 group is such that the O−N−C−H dihedral angle is 0° for one of the hydrogen atoms, although the methyl rotation barrier is very low, as suggested by different ideal geometries at different levels of theory.[53] In the other nitro compound, nitroethene (**13**), similar excellent agreement was observed, with essentially no significant differences between the calculated (C_s) and experimental microwave structures.[54] The calculated structure (C_s) of the remaining compound, methyl

TABLE 2: Calculated (MP2/aug-cc-pVTZ) and Experimental Geometry[a] for Nitromethane, Nitroazide, and Nitroethene[b]

molecule	parameter	calcd	exptl[c]
10	C−N	1.485	1.489
	N−O	1.228,1.230	1.224
	C−H (avg)	1.084	
	O−N−O	125.6	125.3
	O−N−C	117.8,116.6	
	N−C−H[d]	108.2(i), 107.2(o)	107.2
11	C−N	1.474	1.483
	N−N	1.234	1.231
	$N-N_{term}$	1.151	1.137
	C−H (avg)	1.088	1.079
	N−C−H[d]	106.4(i), 111.0(o)	109(i), 112(o)
	N−N−N	173.3	173.1
	N−N−C	114.5	113.9
13	C−N	1.460	1.458
	C−C	1.326	1.325
	N−O	1.227, 1.234	1.227, 1.228
	C−H (avg)	1.079	1.079
	O−N−O	125.5	124.9
	O−N−C	119.0, 115.5	119.1, 116.0
	N−C−H[d]	112.1	112.1
	N−C−C	120.8	120.9
	$C-C-H_{term}$	120.4,119.6	120.2, 119.6

[a] Bond distances are in angstroms, and bond angles are in degrees. [b] Calculated and experimental values for CH_3NH_2 available in ref 34. [c] From microwave spectroscopy: **10**, ref 52; **11**, ref 55; **13**, ref 54. [d] (i) = in plane; (o) = out of plane

TABLE 3: Calculated (MP2/aug-cc-pVTZ) and Experimental Geometry[a] for $HClO_4$ and Phenol

molecule	parameter	calcd	exptl[b]
14	Cl−O	1.406, 1.416(×2)	1.404, 1.414(×2)
	Cl−O	1.643	1.641
	O−H	0.975	0.98
	O−Cl−O	115.2(×2), 113.8	115.0(×2), 114.6
	O−Cl−O	105.0(×2), 100.6	104.2(×2), 101.5
	Cl−O−H	104.8	105.0
16	O−H	0.964	0.958
	C−O	1.370	1.381
	C−C (avg)	1.394	1.399
	C−H (avg)	1.082	1.086
	C−O−H	108.6	106.4
	C−C−O	122.6, 117.1	121.2

[a] Bond distances are in angstroms, and bond angles are in degrees. [b] **14**, combined gas-phase electron diffraction/microwave spectroscopy. ref 56; **16**, electron diffraction, ref 57.

azide (**11**), was in good agreement with experiment. Both structures indicate the NNN segment is nonlinear, with an average angle of 173.2°. The calculated terminal N−N bond distance is overestimated by 0.014 Å, as is the C−N distance by 0.009 Å, compared to the experimental values from microwave spectroscopy.[55]

The calculated structures of $HClO_4$ (**14**) and phenol (**16**), C_6H_6O, are given in Table 3. The experimental structure of **16** was derived from combined gas-phase electron diffraction and microwave experiments.[56] The calculated structure (including tight *d* functions on Cl) of **14** (C_s) is in excellent agreement with the experimental data with no significant differences in the bond distances and angles. The calculated structure of phenol is in good agreement with gas-phase electron diffraction structure.[57] The largest differences are observed in the C−O bond distance (0.011 Å) and C−O−H angle (2.2°). The overall structure is planar with C_s symmetry. The excellent agreement between the theoretical and experimental structures for **1**, **10**, **11**, **13**, **14**, and **16** suggests that the relatively poor agreement between theory and experiment for compound **3** is due to deficiencies in the experiment.

TABLE 4: Calculated Energetic Contributions (kcal/mol) to the Atomization Energy Based on CCSD(T)/CBS Calculations (0 K)

molecule	CCSD(T)/ CBS	$-\Delta E_{ZPE}$	ΔE_{CV}	ΔE_{SR}(DKH)	ΔE_{SO}	ΣD_0 (0K)
1	946.56	−43.42	4.41	−1.33	−0.24	905.99
2	903.30	−34.99	4.08	−1.26	−0.24	870.89
3	816.61	−36.48	3.62	−1.34	−0.16	782.26
4	721.91	−44.75	3.84	−1.42	−0.16	679.41
5	778.93	−27.97	3.30	−1.25	−0.16	752.84
6	666.63	−28.52	2.67	−1.24	−0.08	639.47
7	561.34	−36.81	2.88	−1.33	−0.08	525.99
8	560.75	−37.30	2.90	−1.38	−0.08	524.90
9	643.47	−20.47	2.40	−1.16	−0.08	624.16
10	599.42	−31.13	1.85	−1.07	−0.52	568.55
11	616.44	−31.18	2.34	−0.93	−0.08	586.59
12[a]	580.85	−39.80	1.64	−0.60	−0.08	541.74
13	745.82	−34.15	2.91	−1.27	−0.60	712.71
14	335.35	−17.34	1.14	−3.68	−1.72	313.76
15	342.87	−10.29	1.15	−3.72	−1.72	328.29
16	1465.73	−64.44	6.98	−1.71	−0.70	1405.86
17	1422.56	−55.76	6.73	−1.68	−0.70	1371.16
HN_3	329.19	−13.15	1.29	−0.66	0.00	316.66

[a] From ref 34 and current ΔE_{SR}(DKH) calculation.

The total atomization energies and the components given in eq 3 are reported in Table 4 for all of the molecules and ions (**1**−**17**)

$$\Sigma D_0 = \Delta E_{elec}(CBS) - \Delta E_{ZPE} + \Delta E_{CV} + \Delta E_{SR} + \Delta E_{SO} \quad (3)$$

The atomization energy and its components for molecule **12** were previously calculated but are included in Table 4 for reference.[34] The scalar relativistic correction for **12** has been revised and corresponds to the DKH value.[58] The core valence correction for the entire set of molecules ranges from 1.14 to 6.98 kcal/mol, and in general increases with the number of bonds in the molecule or ion consistent with previous observations.[14] The scalar-relativistic correction for the majority of the molecules and ions is much smaller in magnitude, ranging from −0.6 to −1.71 kcal/mol, excluding $HClO_4$ and ClO_4^-. The scalar relativistic correction for these latter two species is substantially larger at −3.68 and −3.72 kcal/mol, respectively. This can be attributed to the high +7 formal oxidation state of the chlorine atom in both cases, thus resulting in a higher effective nuclear charge. Our scalar relativistic correction for $HClO_4$ is nearly 1 kcal/mol more negative than the recent value reported by Martin of −2.69 kcal/mol at the DK-CCSD(T)/MTsmall level.[59]

The calculated heats of formation at 0 and 298 K are given in Table 5. The heats of formation of 1H-imidazole (**1**) and the imidazolate anion (**2**) are in excellent agreement with the experimental values[60] to within 0.2 kcal/mol. The experimental heat of formation of the imidazolate anion was derived from the deprotonation enthalpy of the imidazole molecule of 350.1 ± 2.1 kcal/mol.[61] The experimental heat of formation of H^+ was taken to be 365.7 kcal/mol.[46] The calculated heat of formation of the imidazolium cation, reported by Dixon and Arduengo,[18] of 171.6 kcal/mol is also in agreement with the experimental value of 172.2 ± 2.0 kcal/mol derived from the proton affinity of imidazole, reported as 225.3 ± 1.9 kcal/mol.[62]

The calculated heats of formation of 1H-1,2,4-triazole (**3**), 1,4-H-1,2,4-triazolium (**4**), and 1,2,4-triazolate (**5**) differ from experiment[60] by only 0.3, 0.2, and 0.5 kcal/mol, respectively. The experimental heats of formation of **4** and **5** were derived

TABLE 5: Calculated and Experimental Heats of Formation at 0 and 298 K (kcal/mol)

	ΔH_f (0 K)		ΔH_f (298 K)	
molecule/ion	calcd	exptl	calcd	exptl
1	35.5		31.6	31.8 ± 0.1[a]
2	19.0		16.0	16.2 ± 2.2[b,c]
3	50.2		46.4	46.1 ± 0.2[a]
4	204.7		199.8	200.0 ± 2.0[c.d]
5	30.0		25.1	24.6 ± 2.3[c,e]
6	83.9		80.2	79.9 ± 1.0[f] 76.7 ± 0.7[g]
7	249.0		244.3	
8	250.1		245.4	
9	47.6		44.8	47.9 ± 3.1[c,e]
10	−13.2	−14.5 ± 0.1[h]	-16.5	−17.9 ± 0.1[h] −19.3 ± 0.3[i]
11	75.9		72.8	
12	−1.4	−1.9 ± 0.2[f,j]	−4.7	−5.4 ± 0.2[f,j]
13	12.6		9.5	9 ± 2[k]
14	5.6[l]		2.8[l]	−1.5[n]
	2.4[m]		−0.4[m]	−2.3[o]
15	−60.4[l]		−63.8[l]	−79.2 ± >14[c,p]
	−63.8[m]		−66.0[m]	
16	−17.2	−18.6 ± 0.2[f,j]	−21.6	−23.0 ± 0.2[f,j]
17	−34.2		−37.8	−38.7 ± 2.2[c,e]
HN_3	72.6	71.8 ± 1.0[q]	71.0	70.3 ± 1.0[q]

[a] Reference 60. [b] Reference 61. [c] Reference 46. [d] Reference 62. [e] Reference 63. [f] Reference 64. [g] Reference 65. [h] Reference 68. [i] Reference 69. [j] Reference 79. [k] Reference 80. [l] From CCSD(T)/aug-cc-pV(D,T,Q) fit based on eq 2. [m] From CCSD(T)/aug-cc-pV(Q,5) fit based on eq 3. [n] References 82 and 83. [o] Reference 84. [p] Reference 85. [q] Reference 78.

from the reported deprotonation enthalpy of 344.2 ± 2.1 kcal/mol[63] and the proton affinity of 211.8 ± 1.9 kcal/mol of molecule **3**,[62] respectively.

The calculated heat of formation of 1H-tetrazole (**6**) at 298 K of 80.2 kcal/mol is in excellent agreement with the reported experimental value of 79.9 ± 1.0 kcal/mol[64] but not the lower value of 76.6 ± 0.7 kcal/mol.[65] A G3(MP2)[66] calculation was also performed,[28] giving a value of 82.8 kcal/mol consistent with our CCSD(T)/CBS result, supporting the higher value. The G3(MP2) heat of formation is in reasonable agreement with our higher level value considering the usual error bar of ∼2 kcal/mol for G3(MP2) heats of formation. These comparisons with experiment and consideration of the errors in each step of the calculations lead us to assign error bars of ±1.0 kcal/mol for the heats of formation.

The calculated heat of formation of the tetrazolate anion **9** of 44.8 kcal/mol is at the lower end of the experimental value obtained from the deprotonation enthalpy of 333.7 ± 3.1 kcal/mol.[63] On the basis of the excellent agreement observed with the 1H-imidazole and 1H-1,2,4-tetrazole heterocycles, these results suggest that the experimental deprotonation enthalpy is in error, and its accurate measurement may possibly be complicated by the existence of the 2H-tetrazole tautomer in the gas phase.[50,67] Experimental proton affinity measurements for 1H-tetrazole in the gas phase are unavailable for comparison to our heats of formation of **7** and **8**, but these values are good to at least ±1 kcal/mol.

The calculated heat of formation at 298 K of CH_3NO_2 (**10**) of −16.5 kcal/mol differs from two reported experimental values of −17.9[68] and −19.3 kcal/mol[69] by 1.4 and 2.8 kcal, respectively. The above calculated value at 298 K also includes a −0.19 kcal/mol correction to the thermodynamic partition function to account for hindered rotation following the method of Pitzer and Gwinn as implemented by Schelegel.[70,71] A single-point CCSD(T)/aug-cc-pV5Z calculation was also performed for **10**, and the CCSD(T)/aug-cc-pV(Q,5)Z energies were extrapolated to the complete basis set limit using eq 3. The heat of formation calculated in this manner yielded a value of −16.3 kcal/mol for $\Delta H_f(CH_3NO_2)$, 0.2 kcal/mol worse than the result from eq 2. This suggests that higher-order correlation corrections may be necessary for molecule **10**. This is surprising as the calculated and experimental values for HNO_3 agree with each other to better than 0.5 kcal/mol and the value of the T_1 diagnostic[72] is not large. The difference for CH_3NO_2 is similar to previous results for NO_2 and HONO, using the same approach, which differed from experiment by ∼1.5 kcal/mol.[20]

The calculated heat of formation at 298 K of CH_3N_3 (**11**) is 72.8 kcal/mol. This is significantly more positive than the value of 57 kcal/mol reported by Franklin et al.[73] from electron impact experiments, as well as the calculated G2 value of 64.5 kcal/mol of Rogers and McLafferty.[74] The value of 75.9 kcal/mol at 0 K is in agreement with the lower level computed value of 73.1 ± 3.0 kcal/mol estimated by Nguyen et al.[75] To test our approach, we also calculated the heat of formation of HN_3 using the same approach (see Table 4). The calculated geometry (Supporting Information) was in good agreement with experiment.[76] The experimental frequencies of HN_3 are known,[77] so we averaged the MP2 values (Supporting Information) with the experimental ones to obtain the zero-point energy correction. The calculated value for $\Delta H_f(HN_3)$ is 72.6 kcal/mol at 0 K and 71.0 kcal/mol at 298 K (Table 5). The both values are in excellent agreement with the experimental values of 71.8 ± 1.0 kcal/mol at 0 K and 70.3 ± 1.0 kcal/mol at 298 K.[78] This excellent agreement shows that our value for CH_3N_3 should be good to ±1 kcal/mol.

Building on previous work,[34] we have calculated the heats of formation of CH_3NH_2 (**12**) at 0 and 298 K based on the reported atomization energy. Our calculated values of −1.4 kcal/mol at 0 K and −4.7 kcal/mol at 298 K using the thermal correction from a MP2/aug-cc-pVTZ calculation are in excellent agreement with the experimental values of −1.9 and −5.4 kcal/mol, respectively.[64,79] The calculated heat of formation of nitroethylene, CH_2CHNO_2 (**13**), of 9.5 kcal/mol at 298 K is also in excellent agreement with the reported experimental value of 9 ± 2 kcal/mol obtained from group additivity considerations.[80]

The heat of formation of $HClO_4$ (molecule **14**) was studied by Martin using W1 and W2 theory.[59] At the W2 level, Martin calculated the heat of formation at 298 K of **14** to be −0.2 kcal/mol, which was revised to a best estimate of −0.6 kcal/mol after additional corrections. Martin noted the importance of tight *d* functions in the basis set to account for the inner shell polarization in this molecule.[81] By use of eq 2 for the extrapolation with the aug-cc-pV(D,T,Q)Z energies, our heat of formation at 298 K for **14** is 2.8 kcal/mol, 3.4 kcal/mol higher than the value reported by Martin.[59] Extrapolation of the CCSD(T)/aug-cc-pV(Q,5) energies using eq 3 lowers the heat of formation by 3.2 kcal/mol to −0.4 kcal/mol and is now in excellent agreement with the results of Martin. Our result is in very good agreement with the reported experimental value of −1.5 kcal/mol determined from the heat of formation of the liquid[82] and its heat of vaporization,[83] although no error bars have been reported to the best of our knowledge. Our results and those of Martin do not support the experimental heat of formation reported by Levy of −2.3 kcal/mol.[84]

We also performed a G3(MP2)[66] heat of formation calculation (results in Supporting Information) on $HClO_4$, which yielded a value of 9.5 kcal/mol at 298 K, nearly 10 kcal/mol higher than our CCSD(T)/CBS result. This clearly suggests that G3(MP2) theory has problems dealing with second-row elements. Our calculations suggest that heat of formation calculations of molecules containing second-row elements in unusually high oxidation states may require very large basis sets (≥ aug-cc-pV5Z) to fully recover the valence correlation energy contribution. In addition, geometry optimizations of these molecules also require basis sets containing additional tight *d* functions, as has been observed by Martin,[59] as well as by us.

Following our procedure for $HClO_4$ using eqs 2 and 3, the calculated heats of formation at 298 K for ClO_4^- (**15**) are −62.6 and −66.0 kcal/mol, respectively. We prefer the latter more negative value based on the above analysis for **14**. The experimental heat of formation −79.2 ± 14 kcal/mol (the error bar is likely greater due to the unreported error bar on the experimental heat of formation of $HClO_4$) for the perchlorate anion was derived from the reported gas-phase acidity of 288.0 ± 14.0 kcal/mol for $HClO_4$.[85] Our calculated value strongly supports an acidity at the higher end of this error range (∼301.2 kcal/mol) and suggests that the intrinsic gas-phase acidity is too low and should be remeasured.

The calculated heat of formation of phenol (**16**) at 298 K is −21.6 kcal/mol. This result is 1.4 kcal/mol higher than the reported experimental value at 298 K of −23.0 ± 0.1 kcal/mol.[64,74] It has been suggested by Feller and Dixon that a higher-order correction of 2.1 kcal/mol is necessary for benzene[14g] to account for the remaining differential correlation energy between the CCSD(T) calculations and a full CI calculation. By assumption that the higher-order correction for **16** is comparable to that of benzene, our calculated result for the heat of formation of **16** at 298 K is −23.7 kcal/mol, well within the desired ±1 kcal/mol accuracy desired. It is noted that the calculated heats of formation with and without the higher-order correction bracket the experimental value. The calculated heat of formation at 298 K of the phenolate anion (**17**) with and without the higher-order correction is −37.8 and −39.9 kcal/mol, respectively. Both values bracket the experimental value of −38.7 ± 2.2 kcal/mol derived from the deprotonation enthalpy of phenol of 350.0 ± 2.0 kcal/mol[63] and are well within the error bar of the measurement.

Conclusions

Ab initio molecular orbital theory at the CCSD(T)/CBS level, including additional corrections for core/valence correlation, scalar relativistic effects, and spin−orbit coupling, has been used to predict the heats of formation of a number of compounds that are relevant to the synthesis of energetic materials, including imidazole-, 1,2,4-triazole-, and tetrazole-based heterocycles, small nitro-, azido-, and amino-compounds, and perchloric acid and phenol. The calculated geometries of the neutral molecules at the MP2 level with triple-ζ quality correlation CBSs are in excellent agreement with the available high quality microwave and gas-phase electron diffraction structures. The heats of formation of the imidazole- and 1,2,4-triazole-based neutrals, cations, and anions agree with the best available experimental data to better than 1 kcal/mol. Our results for tetrazole indicate that the experimental deprotonation enthalpy may be significantly in error, possibly due to experimental evidence with indicates the existence of 1H and 2H tautomers in the gas phase.

The calculated heats of formation of the nitro- and amino-based small molecules, as well as phenol and phenolate, are in excellent agreement with experimental data, although the results for CH_3NO_2 and phenol/phenolate suggest that higher-order corrections on the order of up to 2 kcal/mol may be important. The calculated heat of formation of HN_3 at 0 and 298 K agrees with the experimental values to ±1 kcal/mol, indicating that our calculated CH_3N_3 heat of formation should have similar error bars. The heat of formation of $HClO_4$, derived from a mixed Gaussian/exponential CBS fit of the CCSD(T)/aug-cc-pV(D,T,Q) energies, differed from the experimental value of −1.5 kcal/mol by +4.3 kcal/mol. By use of an extrapolation of the CCSD(T)/aug-cc-pV(Q,5) energies, the heat of formation is improved by 3.2 kcal/mol and differs by only +1.1 kcal/mol error from an experimental value for which no error bars are available. The results for $HClO_4$ and ClO_4^- strongly suggest that extrapolation based on only aug-cc-pV(D,T,Q) energies for molecules with high formal oxidation states of the central atom may be insufficient and that larger basis sets are required. In addition, consistent with literature results, tight *d* functions are necessary to properly describe the geometry due to the high degree of inner shell polarization. Large DKH scalar relativistic corrections are also predicted for $HClO_4$ and ClO_4^- at the MP2 level with correlation consistent DKH basis sets.

Acknowledgment. This work has been supported in part by the Air Force Office of Scientific Research (Grant F49620-03-1-0357). This work has been supported in part by the U.S. Department of Energy's Catalysis Program in the Office of Basic Energy Sciences, Office of Science. This research was performed in part using the Molecular Science Computing Facility (MSCF) in the William R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the U.S. Department of Energy's Office of Biological and Environmental Research and located at the Pacific Northwest National Laboratory. Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle.

Supporting Information Available: Calculated geometries (**2**, **4**, **5**, **6**−**9**, **15**, **17**, and HN_3), calculated and available experimental vibrational frequencies (**1**−**17**, C_2H_4, HN_3), G3-(MP2) energies (**6**,**14**), and MP2 optimized Cartesian coordinates (**1**−**17**, HN_3). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Agrawal, J. P. *Prog. Energy Combust. Sci.* **1998**, *24*, 1.

(2) Drake, G.; Hawkins, T.; Brand, A.; Hall, L.; McKay, M.; Vij, A.; Ismail, I. *Propell. Explos. Pyrot.* **2003**, *28*, 174.

(3) (a) *Ionic Liquids in Synthesis*; Wasserscheid, P., Welton, T., Eds.; VCH−Wiley: Weinheim, 2002. (b) Welton, T. *Chem. Rev.* **1999**, *99*, 2071. (c) Holbrey, J. D.; Seddon, K. R. *Clean Prod. Proc.* **1999**, *1*, 223.

(4) Smiglak, M.; Reichert, W. M.; Holbrey, J. D.; Wilkes, J. S.; Sun, L.; Thrasher, J. S.; Kirichenko, K.; Singh, S.; Katritzky, A. R.; Rogers, R. D. *Chem. Commun.* **2006**, 2554.

(5) Trohalaki, S.; Pachter, R.; Drake, G. W.; Hawkins, T. *Energy Fuels* **2005**, *19*, 279.

(6) Rogers, R. D.; Seddon, K. S. *Science* **2003**, *302*, 792.

(7) (a) Jin, C.-M.; Ye, C.; Piekarski, C.; Twamley, B.; Shreeve, J. M. *Eur. J. Inorg. Chem.* **2005**, 3760. (b) Xue, H.; Arritt, S. W.; Twamley, B.; Shreeve, J. M. *Inorg. Chem.* **2004**, *43*, 7972. (c) Xue, H.; Gao, Y.; Twamley, B.; Shreeve, J. M. *Chem. Mater.* **2005**, *17*, 191. (d) Xue, H.; Shreeve, J. M. *Adv. Mater.* **2005**, *17*, 2142.

(8) (a) Gutowski, K. E.; Holbrey, J. D.; Rogers, R. D.; Dixon, D. A. *J. Phys. Chem. B* **2005**, *109*, 23196. (b) Katritzky, A. R.; Yang, H.; Zhang, D.; Kirichenko, K.; Smiglak, M.; Holbrey, J. D.; Reichert, W. M.; Rogers, R. D. *New J. Chem.* **2006**, *30*, 349.

(9) (a) Katritzky, A. R.; Singh, S.; Kirichemko, K.; Holbrey, J. D.; Smiglak, M.; Reichert, W. M.; Rogers, R. D. *Chem. Commun.* **2005**, 868. (b) Ye, C.; Xiao, J.-C.; Twamley, B.; Shreeve, J. M. *Chem. Commun.* **2005**, 2750. (c) Xue, H.; Twamley, B.; Shreeve, J. M. *J. Mater. Chem.* **2005**, *15*, 3459. (d) Xue, H.; Gao, Y.; Twamley, B.; Shreeve, J. M. *Inorg. Chem.* **2005**, *44*, 5068. (e) Katritzky, A. R.; Singh, S.; Kirichemko, K.; Smiglak, M.; Holbrey, J. D.; Reichert, W. M.; Spear, S. K.; Rogers, R. D. *Chem.−Eur. J.* **2006**, *12*, 4630.

(10) (a) Jenkins, H. D. B.; Roobottom, H. K.; Passmore, J.; Glasser, L. *Inorg. Chem.* **1999**, *38*, 3609. (b) Dixon, D. A.; Feller, D.; Christe, K. O.;

Wilson, W. W.; Vij, A.; Vij, V.; Jenkins, H. D. B.; Olson, R. M.; Gordon, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 834.

(11) Burcat, A. *J. Phys. Chem. Ref. Data* **1999**, *28*, 63.

(12) Byrd, E. F. C.; Rice, B. M. *J. Phys. Chem. A* **2006**, *110*, 1005.

(13) Schmidt, M. W.; Gordon, M. S.; Boatz, J. A. *J. Phys. Chem. A* **2005**, *109*, 7285.

(14) (a) Peterson, K. A.; Xantheas, S. S.; Dixon, D. A.; Dunning, T. H., Jr. *J. Phys. Chem. A* **1998**, *102*, 2449. (b) Feller, D.; Peterson, K. A. *J. Chem. Phys.* **1998**, *108*, 154. (c) Dixon, D. A.; Feller, D. *J. Phys. Chem. A* **1998**, *102*, 8209. (d) Feller, D.; Peterson, K. A. *J. Chem. Phys.* **1999**, *110*, 8384. (e) Feller, D.; Dixon, D. A. *J. Phys. Chem. A* **1999**, *103*, 6413. (f) Feller, D. *J. Chem. Phys.* **1999**, *111*, 4373. (g) Feller, D.; Dixon, D. A. *J. Phys. Chem. A* **2000**, *104*, 3048. (h) Feller, D.; Sordo, J. A. *J. Chem. Phys.* **2000**, *113*, 485. (i) Dixon, D. A.; Feller, D.; Sandrone, G. *J. Phys. Chem. A* **1999**, *103*, 4744. (j) Ruscic, B.; Wagner, A. F.; Harding, L. B.; Asher, R. L.; Feller, D.; Dixon, D. A.; Peterson, K. A.; Song, Y.; Qian, X.; Ng, C.; Liu, J.; Chen, W.; Schwenke, D. W. *J. Phys. Chem. A* **2002**, *106*, 2727. (k) Feller, D.; Dixon, D. A.; Peterson, K. A. *J. Phys. Chem. A* **1998**, *102*, 7053. (l) Dixon, D. A.; Feller, D.; Peterson, K. A. *J. Chem. Phys*. **2001**, *115*, 2576. (m) Pollack, L.; Windus, T. L.; de Jong, W. A.; Dixon, D. A. *J. Phys. Chem. A* **2005**, *109*, 6934. (n) Dixon, D. A.; Gutowski, M. *J. Phys. Chem. A* **2005**, *109*, 5129. (o) Grant, D. J.; Dixon, D. A. *J. Phys. Chem. A* **2005**, *109*, 10138. (p) Alexeev, Y.; Windus, T. L.; Zhan, C.-G.; Dixon, D. A. *Int. J. Quantum Chem.* **2005**, *102*, 775−784. (q) *Int. J. Quantum Chem.* **2005** *104*, 379−380, erratum.

(15) (a) Purvis, G. D., III; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910. (b) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479. (c) Watts, J. D.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 8718.

(16) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

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

(18) Dixon, D. A.; Arduengo, A. J., III. *J. Phys. Chem. A* **2006**, *110*, 1968.

(19) Dixon, D. A.; Francisco, J. S.; Alexeev, Y. *J. Phys. Chem. A* **2006**, *110*, 185.

(20) Dixon, D. A.; Feller, D.; Zhan, C.-G.; Francisco, J. S. *Int. J. Mass. Spectrom.* **2003**, *227*, 421.

(21) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1994**, *100*, 2975.

(22) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6769.

(23) Dunning, T. H., Jr.; Peterson, K. A.; Wilson, A. K. *J. Chem. Phys.* **2001**, *114*, 9244.

(24) Bauschlicher, C. W., Jr.; Partridge, H. *J. Chem. Phys.* **1995**, *240*, 533.

(25) Martin, J. M. L.; Uzan, O. *Chem. Phys. Lett.* **1998**, *282*, 16.

(26) Werner, H.-J.; Knowles, P. J.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Korona, T.; Lindh, R.; Lloyd, A. W.; McNicholas, S. J.; Manby, F. R.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R. M.; Rauhut, G.; Schütz, M.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T. *MOLPRO-2002, a package of initio programs Universität Stüttgart, Stüttgart, Germany*; University of Birmingham: Birmingham, United Kingdom, 2002.

(27) (a) Apra, E.; Bylaska, E. J.; Jong, W. d.; Hackler, M. T.; Hirata, S.; Pollack, L.; Smith, D.; Straatsma, T. P.; Windus, T. L.; Harrison, R. J.; Nieplocha, J.; Tipparaju, V.; Kumar, M.; Brown, E.; Cisneros, G.; Dupuis, M.; Fann, G. I.; Fruchtl, H.; Garza, J.; Hirao, K.; Kendall, R.; Nichols, J. A.; K. Tsemekhman; Valiev, M.; Wolinski, K.; Anchell, J.; Bernholdt, D.; Borowski, P.; Clark, T.; Clerc, D.; Dachsel, H.; Deegan, M.; Dyall, K.; D. Elwood; Glendening, E.; Gutowski, M.; Hess, A.; Jaffe, J.; Johnson, B.; Ju, J.; R. Kobayashi; Kutteh, R.; Lin, Z.; Littlefield, R.; Long, X.; Meng, B.; T. Nakajima; Niu, S.; Rosing, M.; Sandrone, G.; Stave, M.; H. Taylor; G. Thomas; Lenthe, J. v.; Wong, A.; Zhang, Z. *NWChem. PNNL*, **2003**; (b) Kendall, R. A.; Apra, E.; Bernholdt, D. E.; Bylaska, E. J.; Dupuis, M.; Fann, G. I.; Harrison, R. J.; Ju, J.; Nichols, J. A.; Nieplocha, J.; Straatsma, T. P.; Windus, T. L.; Wong, A. T. *Comp. Phys. Comm.* **2000**, *128*, 260−283.

(28) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc., Wallingford CT, 2004.

(29) (a) Møller C.; Plesset M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1.

(30) Rittby, M.; Bartlett, R. J. *J. Phys. Chem.* **1988**, *92*, 3033.

(31) Knowles, R. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1994**, *99*, 5219.

(32) Deegan, M. J. O.; Knowles, P. J. *Chem. Phys. Lett.* **1994**, *227*, 321.

(33) Peterson, K. A.; Woon. D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1994**, *100*, 7410.

(34) Feller, D.; Dixon, D. A. *J. Chem. Phys.* **2001**, *115*, 3484.

(35) (a) Martin, J. M. L. *Chem. Phys. Lett.* **1996**, *259*, 669. (b) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, *106*, 9639. (c) Halkier, A.; Helgaker, T.; Jørgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. L. *Chem. Phys. Lett.* **1998**, *286*, 243. (d) Klopper, W.; Bak, K. L.; Jørgensen, P.; Olsen, J.; Helgaker, T. *J. Phys. B* **1999**, *32*, R103.

(36) (a) Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **2002**, *117*, 10548. (b) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.

(37) (a) Douglas, M.; Kroll, N. M. *Ann. Phys.* **1974**, *82*, 89. (b) Hess, B. A. *Phys. Rev. A* **1985**, *32*, 756. (c) Hess, B. A. *Phys. Rev. A* **1986**, *33*, 3742.

(38) de Jong, W. A.; Harrison, R. J.; Dixon, D. A. *J. Chem. Phys.* **2001**, *114*, 48.

(39) EMSL basis set library. http://www.emsl.pnl.gov/forms/basisform.html

(40) Moore, C. E. *Atomic energy levels as derived from the analysis of optical spectra*; U.S. National Bureau of Standards Circular 467; U.S. Department of Commerce, National Technical Information Service: Washington, DC, 1949; No. COM-72-50282, Vol. 1H−V.

(41) (a) Wells, A. J.; Wilson, E. B., Jr. *J. Chem. Phys.* **1941**, *9*, 314. (b) Jones, W. J.; Sheppard, *N. Proc. R. Soc. A* **1968**, *304*, 135.

(42) Durig, D. T.; Durig, M. S.; Durig, J. R. *Spec. Chim. Acta A* **2005**, *61*, 1287.

(43) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies, Consolidated Volume 1*; U.S. National Bureau of Standards: Washington, DC, NSRDS NBS-39, 1972.

(44) Karelin, A. I.; Grigorovich, Z. I.; Rosolovskii, V. Y. *Spec. Chim. Acta A*, **1975**, *31*, 765.

(45) Michalska, D.; Bieñko, D. C.; Abkowicz-Bieñko, A. J.; Latajka, Z. *J. Phys. Chem.* **1996**, *100*, 1786.

(46) Chase, M. W., Jr. *J. Phys. Chem. Ref. Data* **1998**, *Monograph 9*, Suppl. 1.

(47) Christen, D.; Griffiths, J. H.; Sheridan, J. *Z. Naturforsch. A* **1982**, *37*, 1378.

(48) Bolton, K.; Brown, R. D.; Burden, F. R.; Mishra, A. *J. Mol. Struct.* **1975**, *27*, 261.

(49) Chiang, J. F.; Lu, K. C. *J. Mol. Struct.* **1977**, *41*, 223.

(50) Mazurek, A. P.; Osman, R. *J. Phys. Chem.* **1985**, *89*, 460.

(51) Krugh, W. D.; Gold, L. P. *J. Mol. Spectrosc.* **1974**, *49*, 423.

(52) Cox, A. P.; Waring, S. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1060.

(53) http://srdata.nist.gov/cccbdb/

(54) Nossberger, P.; Bauder, A.; Gunthard, H.-H. *Chem. Phys.* **1975**, *8*, 245.

(55) Heineking, N.; Gerry, M. C. L. *Z. Naturforsch. A* **1989**, *44*, 669.

(56) Casper, B.; Mack, H.-G.; Müller, H. S. P.; Willner, H.; Oberhammer, H. *J. Phys. Chem.* **1994**, *98*, 8339.

(57) Portalone, G.; Schultz, G.; Domenicano, A.; Hargittai, I. *Chem. Phys. Lett.* **1992**, *197*, 482.

(58) Bauschlicher, C. W., Jr. *J. Phys. Chem A* **2000**, *104*, 2281.

(59) Martin, J. M. L. *THEOCHEM* **2006**, *771*, 19.

(60) Jiminez, P.; Roux, M. V.; Turrion, C. *J. Chem. Therm.* **1987**, *19*, 985.

(61) Taft., R. W.; Anvia, F.; Taagepera, M.; Catalan, J.; Elgueroy, J. *J. Am. Chem. Soc.* **1986**, *108*, 3237.

(62) Hunter, E. P.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.

(63) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. Neutral Thermochemical Data. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg MD, 20899, 2005 (http:// webbook.nist.gov).

(64) Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; Thermodynamic Research Center: College Station, TX, 1994; Vol. I.

(65) Balepin, A. A.; Lebedev, V. P.; Miroshnichenko, E. A.; Koldobskii, G. I.; Ostovskii, V. A.; Larionov, B. P.; Gidaspov, B. V.; Lebedev, Y. A. *Svoistva Veshchestv Str. Mol.* **1977**, 93.

(66) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1999**, *110*, 4703.

(67) Palmer, M. H.; Simpson, I.; Wheeler, J. R. *Z. Naturforsch. A* **1981**, *36*, 1246.

(68) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data, Supp. 2* **1982**, *11*, 1.

(69) Knobel, Y. K.; Miroshnichenko, E. A.; Lebedev, Y. A. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1971**, 425.

(70) Pitzer, K. S.; Gwinn, W. D. *J. Chem. Phys.* **1942**, *10*, 428.

(71) Ayala, P. Y.; Schlegel, H. B. *J. Chem. Phys.* **1998**, *108*, 2314.

(72) Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem.* **1989**, *S23*, 199.

(73) Franklin, J. L.; Dibeler, V. H.; Reese, R. M.; Krauss, M. *J. Am. Chem. Soc.* **1958**, *80*, 298.

(74) Rogers, D. W.; McLafferty, F. J. *J. Chem. Phys.* **1995**, *103*, 8302.

(75) Nguyen, M. T.; Sengupta, D.; Ha, T.-K. *J. Phys. Chem.* **1996**, *100*, 6499.

(76) Winnewisser, B. P. *J. Mol. Spectrosc.* **1980**, *82*, 220.

(77) Shimanouchi, T. *J. Phys. Chem. Ref. Data* **1977**, *103*, 993.

(78) Gurvich, L. V.; Veyts, I. V.; Alcock, C. B. *Thermodynamic Properties of Individual Substances*, 4th ed.; Hemisphere Pub. Co.: New York, 1989.

(79) Frenkel, M.; Kabo, G. J.; Marsh, K. N.; Roganov, G. N.; Wilhoit, R. C. *Thermodynamics of Organic Compounds in the Gas State*; Thermodynamic Research Center: College Station, TX, 1994; Vol. II.

(80) Luo, Y.-R.; Holmes, J. L. *J. Phys. Chem.* **1992**, *96*, 9568.

(81) Boese, A. D.; Martin, J. M. L. *J. Mol. Struct.* **2006**, *780−781*, 310.

(82) *CRC Handbook of Chemistry and Physics*, 86th ed.; Lide, D. R., Ed.; CRC Press LLC: Boca Raton, FL, 2005−2006.

(83) Colussi, A. J.; Grela, M. A. *J. Phys. Chem.* **1993**, *97*, 3775.

(84) Levy, J. B. *J. Phys. Chem.* **1962**, *66*, 1092.

(85) Marcus, Y. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 339.