J. Phys. Chem. A **2007,** *111,* 5743−5750

Application of the Computationally Efficient Self-Consistent-Charge Density-Functional Tight-Binding Method to Magnesium-Containing Molecules[†]

Zheng-Li Cai,[‡] Philip Lopez,[‡] Jeffrey R. Reimers,[‡] Qiang Cui,[§] and Marcus Elstner[#]

School of Chemistry, The University of Sydney, NSW 2006, Australia, Department of Chemistry and Theoretical Chemistry Institute, University of Wisconsin—Madison, Madison, Wisconsin 53706, Theoretical Physics, Faculty of Science, University of Paderborn, D-33098 Paderborn, Germany, and Department of Physical and Theoretical Chemistry, TU Braunschweig, D-38106 Braunschweig, Germany

Received: March 1, 2007; In Final Form: May 19, 2007

The geometric properties, ionization potentials, heats of formation, incremental binding energies, and protonation energies for up to 75 magnesium-containing compounds have been studied using the self-consistent-charge density-functional tight-binding method (SCC-DFTB), the complete-basis set (CBS-QB3) method, traditional B3LYP density-functional theory, and a number of modern semiempirical methods such as Austin Model 1 (AM1), modified neglect of diatomic overlap without and with inclusion of d functions (MNDO, MNDO/d), and the Parametric Method 3 (PM3) and its modification (PM5). The test set contains some widely varying chemical motifs including ionic or covalent, closed-shell or radical compounds, and many biologically relevant complexes. Geometric data are compared to experiment, if available, and otherwise to previous high-level ab initio calculations or the present B3LYP results. SCC-DFTB is found to predict bond lengths to high accuracy, with the root-mean-square (RMS) error being less than half that found for the other semiempirical methods. However, SCC-DFTB performs very poorly for absolute heats of formation, giving an RMS error of 29 kcal mol^{-1}, but for this property B3LYP and the other semiempirical methods also yield poor but useful results with errors of 12−22 kcal mol^{-1}. Nevertheless, SCC-DFTB does provide useful results for biologically relevant chemical-process energies such as protonation energies (RMS error 10 kcal mol^{-1}, with the range 6−19 kcal mol^{-1} found for the other semiempirical methods) and ligation energies (RMS error 9 kcal mol^{-1}, less than the errors of 12−23 kcal mol^{-1} found for the other semiempirical methods). SCC-DFTB is shown to provide a computationally expedient means of calculating properties of magnesium compounds, providing results with at most double the inaccuracy of the high-quality but dramatically more-expensive B3LYP method.

1. Introduction

The density-functional tight-binding (DFTB) method has been developed as a second-order approximation to density functional theory (DFT).[1] It is an efficient electronic-structure computational algorithm that is well-suited to computations on large molecular systems. Recently, an enhanced version of this method involving self-consistent charge description, the self-consistent-charge density-functional tight-binding method (SCC-DFTB), has emerged. This enhancement significantly improves the transferability and generality of this approach through the proper treatment of intramolecular charge flow and polarization.[2] Application of the method requires the specification of a variety of parameters per atom and per atom pair. These parameters are obtained directly from the results of density-functional calculations using Becke's three-parameter hybrid exchange functional coupled with Lee−Yang−Parr correction functional (B3LYP), establishing the SCC-DFTB method as a rigorously defined approximation to this first-principles computational technique. To date, the required parameters have been calculated for the atoms H, C, N, O, P, S, and Zn.[3,4] SCC-DFTB predictions of molecular properties including energies, geometries and vibrational frequencies of small organic molecules, hydrogen-bonded complexes, DNA bases, Schiff bases, peptides, and fullerenes[2−15] have been in excellent agreement not only with those predicted by full B3LYP calculations but also with experimental results. Here we present an extension of the method to include Mg, demonstrating the appropriateness of the method to electronic-structure evaluation through investigation of the properties of 75 compounds containing H, C, N, O, S, P, and Mg atoms; preliminary parameters are also presented describing phosphorus P−H interactions. The molecular test set includes small inorganic complexes, organometallic complexes, and various biologically relevant molecules such as chlorophylls, and ligated species including $Mg^{2+}[X]_n$ with X = H_2O, NH_3, SH_2, PH_3, CO for $n = 1-4$ and X = OH, SH, NH_2, PH_2, CH_3 for n = 1 and 2.

An attractive feature of the SCC-DFTB method is that it is intrinsically very much more computationally efficient than is B3LYP DFT and other a priori density-functional approaches. However, a variety of other approximate computational schemes is also available for the rapid evaluation of electronic structure using approximate computational methods. The most popular of these are the semiempirical techniques such as Austin Model 1 (AM1),[16] modified neglect of diatomic overlap with inclusion of d functions (MNDO/d),[17] the Parametric Method 3 (PM3),[18] and its latest modification (PM5); all of these approaches are based on the Hartree−Fock (HF) theory. Methods of this type are currently experiencing a renaissance, being applied to a

---

[†] Part of the "DFTB Special Section".

[‡] The University of Sydney.

[§] University of Wisconsin—Madison.

[#] University of Paderborn and TU Braunschweig.

10.1021/jp071701m CCC: $37.00

wider range of phenomena, and are also being developed for some important specific applications as well as general usage.[19] In terms of computational implementation, SCC-DFTB and these other semiempirical methods appear similar. Advances such as the linear scaling techniques that have allowed semiempirical methods to treat tens of thousands of atoms can also be applied to SCC-DFTB, meaning that intrinsically all of these methods require the same order of magnitude of computational time to solve any particular problem. Also, as SCC-DFTB is a simplification of DFT, any advances made in linear scaling or similar approaches to DFT may also be applied to it. Collectively, semiempirical methods will thus remain at the forefront for calculations on large biological, chemical, and materials systems.

A significant conceptual difference distinguishes SCC-DFTB from these other more traditional semiempirical approaches. Though all methods afford well-defined approximations to first-principles computational schemes, AM1, PM3, MNDO, MNDO/d, and the like are built upon ad hoc approximations. However, all of the parameters required to perform SCC-DFTB calculations on any molecular system are specified by a predetermined algorithm, and an internally consistent parametrization of the entire periodic table is, in principle, feasible and straightforward. Note, however, that this algorithm does require the specification of molecules for which the calculations that determine the SCC-DFTB parameters are performed and hence a single unique parametrization cannot be obtained for any interaction. Nevertheless, this situation is quite different from that arising for the other semiempirical methods, as these the parameters are determined by fitting to experimental data for the selected molecules. This is an involved procedure for any atom, with the results being actually quite sensitive to the molecular data set used to train the parameters. An internally consistent parametrization for all atoms is not possible to obtain, with the best efforts to achieve such consistency requiring the simultaneous fitting of all parameters for all atoms.[17] Indeed, there have been two[20,21] AM1 parametrizations of Mg.

However, it is not self-evident that the closer links between SCC-DFTB and a first-principles computational scheme should lead to improved predictions of molecular properties, as the alternate methods are fitted to reproduce experimental data. Once a method is established, it is this rather than issues of relative efficiency that will determine its robustness and the usefulness. Hence we compare molecular properties predicted by SCC-DFTB to those predicted by AM1 (in both its old[20] and new[21] parametrizations), PM3, PM5, MNDO/d,[17] and MNDO.[21,22] The properties considered include bond lengths, bond angles, ionization potentials (IP), heats of formation ΔH^{f}, incremental ligand binding energies $-\Delta\Delta E$ (these quantities are actually used in the DTFB parametrizaton), and protonation energies $-\Delta E^{\mathrm{H}}$. We also make extensive comparisons with results obtained directly using B3LYP[23] as well as with results from either high-level calculations or experiment. The high-level methods used include either second-order Möller−Plesset (MP2) perturbation theory[24] or quadratically convergent configuration-interaction singles and doubles (QCISD) theory[25] for geometry optimizations and the complete basis set extrapolation developed by Petersson and co-workers, CBS-QSB3,[26−29] for energies. The test data set used included 38 molecules used in previous semiempirical studies of magnesium chemistry as well as 37 additional molecules involving biologically relevant ligation processes, making a complete test set of 75 molecules. Note that many of these molecules appeared in the training sets used in the parametrization of AM1,[20] PM3,[18] MNDO,[21,22] and MNDO/d,[17] to reproduce experimental and high-level computational data, and others were used in the test set for fitting of the SCC-DFTB parameters to B3LYP potentials.

2. Methods

A. Reference Properties of the 75-Molecule Test Set. The test set is composed of the 38 molecules containing Mg and possibly only H, C, N, O, and S used in a previous comparative study of the properties of the AM1, PM3, and MNDO/d methods,[20] augmented if necessary additional biological relevant ligated magnesium species of the form $\mathrm{Mg}^{2+}[\mathrm{X}]_n$ with X = H_2O, NH_3, SH_2, PH_3, CO for $n = 1-4$ and X = OH, SH. NH_2, PH_2, CH_3 for $n = 1$ and 2. Reference data for this test set is taken from experiment,[30−36] where available, but as this information is limited, alternate strategies are developed. For most molecules, reference geometric data is available[37,38] at either the MP2/6-31++G** or QCISD/6-311++G** levels or is calculated in this work using MP2/6-31++G**; for the remaining molecules, reference geometries are taken from the results of B3LYP/6-311++G** calculations. Reference data for all reaction energies not available experimentally are determined at the CBS-QB3 level.[26−29] Note that the geometries used as part of the CBS-QB3 calculations are obtained using B3LYP with a smaller basis set than that used in our own B3LYP calculations and hence are not discussed directly; the differences in basis set are small, however, as CBS-QB3 employs the CBS7 basis set containing the s and p orbitals from 6-31G combined with the polarization functions from 6-311**.

B. SCC−DFTB, AM1, PM3, PM5, MNDO, MNDO/d, B3LYP, and CBS-QB3 Calculations of Electronic Structures. The following methods were used for the evaluation of electronic structures: (1) the SCC-DFTB[2] method using the deduced parameters for Mg and its interactions, (2) the B3LYP[23] density functional with the 6-311++G** basis set[39,40] using the GAUSSIAN-03 package,[41] (3) AM1[16] calculations with both the old[20] Mg parameters using the VAMP[42] or GAUSSIAN-98[43] packages and the new[21] Mg parameters using GAUSSIAN-03,[41] (4) MNDO/d,[17] MNDO,[21,22] PM3,[18,21] and PM5 calculations using the MOPAC 2002 package,[44] and (5) CBS-QB3[26−29] calculations performed using GAUSSIAN-03.[41]

C. Parametrization of the SCC−DFTB Method for Mg and Its Interaction with H, C, N, O, P, and S. The SCC-DFTB method, developed by Elstner et al. and described in detail elsewhere,[2] is derived from density functional theory by expanding the total energy functional up to second order with respect to charge density fluctuations around the reference density. A repulsive contribution, which models the DFT double-counting energy terms, as well as a core−core repulsion contribution, comprise the DFTB total energy, and the parametrization procedure for Mg used herein follows that specified previously[4] for the parameterzation of Zn. The determination of the parameters for the first term requires the calculation of the Hamilton and overlap matrix elements using DFT. To do so, one has to specify a confinement radius for the atomic orbitals and a confinement radius for the input density.[2,4] For Mg, these values are taken to be 5.0 Å for the s and p orbitals and 12 Å for the confinement of the initial density of the Mg atom.[2,4]

For the parametrization of the repulsive potential, we have to calculate the dissociation potential of every possible Mg−X bond (X = H, C, N, O, P, S) using suitable chosen test molecules. Here, we used the indicated bonds of the following molecules: HMg−H, HMg−NH_2, HMg−OH, HMg−CH_3, HMg−PH_2, and HMg−SH. Because the bonds cannot be

TABLE 1: Statistical Analysis of the Comparison (Table S1) of Geometrical Variables for All Molecules in the Test-Set

property	statistic	comparing MP2/QCISD[b] to experiment[c]	comparing B3LYP to MP2/QCISD[b]	comparing reference data to[a]						
					AM1					
				SCC-DFTB	new	old	PM3	MNDO	MNDO/d[d]	PM5
bond lengths/Å	mean error	0.004	0.005	0.011	−0.031	−0.057	−0.103	−0.050	−0.099	−0.056
	mean absolute error	0.007	0.012	0.032	0.079	0.102	0.136	0.067	0.120	0.070
	standard deviation	0.010	0.018	0.042	0.108	0.122	0.142	0.087	0.106	0.079
	RMS error	0.010	0.019	0.043	0.112	0.135	0.176	0.100	0.145	0.097
	no. of comparisons	5	53	78	79	79	79	73	79	73
	no. unbound	0	0	0	0	0	1	6	0	6
bond angles/deg	mean error		−0.6	0.2	−0.4	−1.3	−2.7	1.1	2.2	−0.7
	mean absolute error		1.9	3.7	2.0	3.4	6.3	3.5	3.7	1.8
	standard deviation		4.0	7.1	3.6	5.2	9.7	7.4	7.9	3.2
	RMS error		4.1	7.1	3.7	5.4	10.1	7.5	8.2	3.3
	no. of comparisons		46	92	97	87	82	80	93	87
	no. of bad conformations		0	5	0	10	15	7	4	0
symmetry	no. incorrect		0	2	2	3	5	2	2	2

[a] Experiment if available; otherwise, MP2/QCISD if available; otherwise, B3LYP/6-311++G**; for other calculations see refs 20 and 54−58. [b] From refs 37 and 38. [c] From refs 30−36 and 68 or this work MP2/6-311++G**. [d] From ref 20.

TABLE 2: Comparison of Calculated and Observed Vertical Ionization Potentials (eV)

molecule	wiht motional corrections								without corrections		
			AM1								
	experiment	CBS-QB3	new	old	PM3	MNDO	MNDO/d	PM5	CBS-QB3	B3LYP	SCC-DFTB
Mg	7.65[a]	7.59	7.98	7.47	7.93	7.84	7.72	7.80	7.59	7.73	7.76
Mg^+	15.04[a]	14.96	14.67	14.97	14.62	14.81	15.10	14.91	14.96	15.56	13.87
$Mg(C_5H_5)_2$	8.06[b]	8.06	8.33	8.32	8.36	8.21	8.79	8.11	8.13	7.86	8.02
Mg porphyrin	6.46[c,d]/6.44[c,e]	6.63	7.31	7.27	7.61	7.28	7.13	7.25	6.71	6.84	7.04
mean error		0.01	0.27	0.21	0.33	0.24	0.39	0.22		0.15	−0.18
mean absolute error		0.08	0.46	0.33	0.54	0.35	0.39	0.28		0.29	0.43
standard deviation		0.11	0.44	0.39	0.56	0.38	0.32	0.36		0.31	0.55
RMS error		0.11	0.52	0.45	0.65	0.45	0.50	0.42		0.34	0.58
no. of comparisons		4	4	4	4	4	4	4		4	4

[a] From ref 59. [b] From ref 60. [c] From ref 20. [d] Vertical ionization energy, used as reference for comparison. [e] Adiabatic ionization energy.

TABLE 3: Statistical Analysis of the Comparison (Table S2) of Calculated Heats of Formation (kcal mol^{-1})[a]

molecules	property	CBS-QB3	AM1		PM3	MNDO	MNDO/d	PM5	B3LYP	SCC-DFTB
			new	old						
with Mg	mean error	0.8	−1.0	1.8	−6.5	−9.8	5.9	−0.8	1.5	−0.2
	mean absolute error	4.0	13.9	13.1	15.4	13.4	13.7	8.5	11.6	19.4
	standard deviation	5.0	20.1	16.3	20.5	16.9	17.8	12.0	18.1	29.0
	RMS error	5.0	20.1	16.4	21.5	19.5	18.7	12.0	18.2	29.0
	no. of comparisons	6	54	53	54	48	54	48	54	54
without Mg	mean error	−0.8	2.3	5.1	1.0	2.2	4.0	−4.0	7.5	14.0
	mean absolute error	1.0	12.8	14.4	8.0	13.7	13.4	11.0	7.5	16.2
	standard deviation	1.2	17.5	18.8	9.2	17.3	16.4	17.8	2.9	13.5
	RMS error	1.4	17.6	19.5	9.2	17.4	16.9	18.2	8.1	19.5
	no. of comparisons	12	16	15	16	16	15	16	16	15

[a] CBS-QB3 is compared to experiment and the other methods are compared to experiment,[59−66] if available, or otherwise, CBS-QB3. For other calculations see refs 17, 30, 54, and 67.

stretched until the dissociation limit is reached, the binding energy cannot be determined in this step to a sufficient accuracy. Further calculations are therefore needed to calibrate the total energy. Practically, this is done by optimizing the repulsive potential with respect to binding energies of suitable complexes. The emphasis of this parametrization is on the simulation of magnesium in biological systems in environments where Mg is usually coordinated by several ligands. We therefore optimized the repulsive potential to yield good incremental binding energies, as shown later in Table 5. This second step in the parametrization has no influence on the properties of the first one, because the repulsive potential is shifted in energy as a whole, whereas the curvature and slope are not changed in the binding region; i.e., optimized geometries are not influenced by this step. Some disconnection between the ability of DFTB to predict accurate geometries and its ability to predict accurate binding energies at these geometries can thus be expected. The main emphasis was to reproduce the higher-coordinated complexes, rather than the lower-coordinated ones. Therefore, in subsequent discussions, Table 5 is not shown as a test for the method but rather to illustrate the performance of DFTB for the fitting molecular data set.

D. Geometry Optimizations. The initial geometries were derived from experimentally observed structures where possible, otherwise appropriate calculated geometries were employed. As it is possible that these structures are not local minima but rather high-symmetry transition states on the SCC-DFTB potential-energy surface, the nuclear coordinates were randomized in most cases by up to 0.3 Å prior to optimization. In addition, alternate initial structures for some molecules were also used that depicted feasible molecular isomers. To optimize the geometries, a steepest-descent relaxation procedure was initially used, fol-

TABLE 4: Experimental and Effective Atomic Heats of Formation for SCC-DFTB and B3LYP/6-311++G**

		B3LYP/6-311++G**		SCC-DFTB	
atom	experimental ΔH^{f}	correction	optimized ΔH^{f}	correction	optimized ΔH^{f}
H	52.102	6.98	59.08	28.3147	80.4167
C	170.89	4.2	175.09	39.7828	210.6728
N	113	3.58	116.58	89.5856	202.5856
O	59.559	3.09	62.649	46.263	105.822
Mg	35	−20.71	14.29	−2.57	32.64
P	75.57	1.51	77.08	34.00	109.57
S	66.4	1.56	67.96	36.05	101.70

lowed by a conjugate gradient relaxation. Only the lowest-energy structures obtained are reported in the subsequent tables; symmetry is reported explicitly only when different methods yield alternative results.

E. Ionization Energies. Ionization potentials were evaluated from the total energies of the molecule(s) and their ion(s).

F. Heats of Formation ΔH^{f}. Heats of formation are calculated as part of the CBS-QB3 computational procedure using

$$\Delta H^{\mathrm{f}} = E_{\mathrm{molecule}} - \sum_{\mathrm{atoms}} (E_{\mathrm{atoms}} - \Delta H^{\mathrm{f}}_{\mathrm{atoms}}) + E_{\mathrm{motion}} \qquad (1)$$

where E_{molecule} is the total electronic energy, $\Delta H^{\mathrm{f}}{}_{\mathrm{atoms}}$ is the experimental heat of formation of the atom, and E_{motion} is the sum of the zero-point energy and thermal correction appropriate for 298 K. For B3LYP and semiempirical methods,[45−50] it is usual not to evaluate the motional correction explicitly for each molecule but rather to parametrize the method either to neglect this term altogether or to add a fixed correction term per atom of each type:

$$\Delta H^{\mathrm{f}} = E_{\mathrm{molecule}} - \sum_{\mathrm{atoms}} (E_{\mathrm{atoms}} - \Delta H^{\mathrm{f}}_{\mathrm{atoms}} + E^{\mathrm{corr}}_{\mathrm{atoms}}) \qquad (2)$$

This later approach has been successfully applied to SCC-DFTB[45−49] and is adopted herein. We use the previously determined by Sattelmeyer et al.[49] corrections for H, C, N, O, and S and determine corrections for P (tentative only) and Mg. For B3LYP/6-311++G** we use the correction terms determined recently by Winget and Clark[50] for H, C, N, O, P, and S and determine the value for Mg.

G. Incremental Ligand Binding Energies $-\Delta\Delta E$ and Protonation Energies $-\Delta E^{\mathrm{H}}$. The incremental binding energies for ligand X and deprotonation energies are evaluated using the CBS-QB3 method, a method that takes into account explicit corrections for thermal or zero-point motion, based on the following reactions:

$$\mathrm{Mg}^{2+}\mathrm{X}_n + \mathrm{X} \rightarrow \mathrm{Mg}^{2+}\mathrm{X}_{n+1} \qquad (3)$$

and

$$\mathrm{Mg}^{2+}\mathrm{X}^- + \mathrm{H}^+ \rightarrow \mathrm{Mg}^{2+}\mathrm{XH} \qquad (4)$$

respectively, where X is a neutral or charged ligand. For AM1, PM3, MNDO, MNDO/d, and PM5, implicit correction for motional effects have been included into their parametrizations and hence raw energies obtained using these methods are compared directly with the experimental and CBS-QB3 results. However, B3LYP and SCC-DFTB total energies do not include implicit motional corrections and hence their differences cannot be directly compared to the experimental data. So as to focus on the energies predicted by these methods rather than the accuracy of their associated vibration frequencies, we choose to compare B3LYP and SCC-DFTB results to those obtained by subtracting the motional contributions from the total CBS-QB3 energy.

3. Results and Discussion

A. Geometries, Bond Lengths, and Bond Angles. A detailed comparison of the calculated SCC-DFTB, AM1, PM3, MNDO, MNDO/d, and PM5 geometrical variables (geometries, bond lengths, and bond angles) with those of the reference data is provided in Supporting Information in Table S1, and a statistical summary is given in Table 1. Only bond lengths and bond angles involving Mg are included in the statistical summary.

Only five bond lengths involving Mg are available experimentally, and for these the MP2 and QCISD reference methods predict structures with an average error and root-mean-square (RMS) error of just 0.004 and 0.010 Å, respectively. For the 53 bond lengths studied using these computational methods and B3LYP/6-311+G**, the mean difference is 0.005 Å and the RMS error is 0.019 Å. This indicates that there exists a high degree of consistency in the results predicted by the various reference methods, as is expected.[51] Good agreement is also seen between the MP2 or QCISD and B3LYP/6-311+G** Mg-containing bond angles, with an average discrepancy of −0.6° and an RMS error of 4.1°. Most significantly, both methods predict the same structural conformations for the molecules. Of the semiempirical methods, AM1 (new parametrization) and PM5 both predict the anticipated conformations; SCC-DFTB and the old AM1 parameters predict that Mg−O−H bonds are bent instead of linear, however, and a range of conformational anomalies are predicted by PM3 and MNDO/d. Table 1 tallies the total number of variant conformations predicted by the semiempirical methods, but differences in bond angle are counted only for structures with the same conformation. Also shown in the table are the number of optimized structures with variant point-group symmetries, these variations reflecting both the above conformational changes as well as the orientations of ligands with respect to each other. SCC-DFTB performs comparably with the other methods in its ability to predict symmetry, with PM3 providing predictions that are notably poor. For bond angles within the same conformer, SCC-DFTB has average and RMS differences from the reference data of 0.2° and 7.1°, respectively. Although such deviations are significant, the accuracy achieved will be sufficient for many purposes. Of the other semiempirical methods considered, AM1 and PM5 show about half of this discrepancy but it is of the same order for MNDO, MNDO/d, and PM3. However, the SCC-DFTB bond lengths differ from the reference data by an average of just 0.011 Å with an RMS error of 0.043 Å, results that are significantly better than those from all other semiempirical methods. PM3 consistently provides the poorest geometrical estimates. The revised AM1 parameters provide better conformational depiction, slightly poorer bond lengths, and slightly better bond angles compared to the original parametrization, whereas the new MNDO parameters provide better bond lengths but poorer angles and conformational information.

The bond-length statistics shown in Table 1 exclude results obtained for the diatomic Mg_2 molecule. For this, the observed[37] bond length is very long, 3.89 Å, and quite expectedly the computational methods predict a wide range of bond lengths ranging from unbound (PM3) to 2.7 Å (MNDO/d). MP2 predicts 4.31 Å, B3LYP 3.94 Å, and SCC-DFTB 4.30 Å. These results suggest that SCC-DFTB warrants attention as a possible efficient method for studying magnesium clusters, surface, and solids, but such an investigation is outside the scope of this work.

TABLE 5: Calculated Incremental Ligand Binding Energies $-\Delta\Delta E$ (Eq 3), in kcal mol^{-1}, and the Statistical Comparison of Differences with the CBS Results[a]

	with motional corrections									
		AM1							without corrections	
product	CBS-QB3	new	old	PM3	MNDO	MNDO/d	PM5	CBS-QB3	B3LYP	SCC-DFTB
$Mg^{2+}(H_2O)_2$	68.9	71.1	62.0	67.6	55.6	68.7	66.4	71.2	74.0	75.2
$Mg^{2+}(H_2O)_3$	55.7	58.6	52.0	58.2	44.7	57.3	54.7	58.3	58.3	61.6
$Mg^{2+}(H_2O)_4$	45.7	47.1	45.0	49.1	29.4	47.9	44.8	48.2	47.6	48.1
$Mg^{2+}(SH_2)_2$	58.1	66.4	72.0	61.4	68.4	69.6	54.6	60.4	61.9	53.8
$Mg^{2+}(SH_2)_3$	41.0	49.4	58.0	53.5	55.1	50.0	38.3	43.2	40.8	39.0
$Mg^{2+}(SH_2)_4$	31.6	36.5	46.0	42.7	44.7	38.0	28.5	33.9	30.9	31.7
$Mg^{2+}(NH_3)_2$	79.5	92.8	88.0	87.3	86.4	74.8	90.2	82.0	84.7	73.2
$Mg^{2+}(NH_3)_3$	59.4	76.3	74.0	75.2	72.9	58.5	73.7	62.3	61.2	57.6
$Mg^{2+}(NH_3)_4$	46.1	61.1	64.0	64.0	58.3	47.8	58.2	49.5	47.4	47.4
$Mg^{2+}(PH_3)_2$	63.0	54.4	64.0	80.1		63.8		65.6	67.0	57.9
$Mg^{2+}(PH_3)_3$	43.8	43.0	46.0	56.2		45.7		46.1	41.5	38.8
$Mg^{2+}(PH_3)_4$	30.7	35.7	36.0	38.6		38.7		33.1	31.0	31.3
$Mg^{2+}(CO)_2$	42.0	73.9	73.0	53.9	85.9	82.6	71.3	44.1	45.9	41.6
$Mg^{2+}(CO)_3$	32.9	65.5	66.0	45.2	75.3	70.7	60.0	34.8	32.5	34.5
$Mg^{2+}(CO)_4$	29.0	53.3	58.0	37.4	64.1	60.0	49.0	31.1	57.2	30.2
$Mg(OH)_2$	240.2	237.8	244.0	243.0	240.4	259.4	216.9	242.0	241.2	250.5
$Mg(SH)_2$	197.7	205.7	231.0	195.3	212.1	216.2	187.2	199.2	196.1	230.1
$Mg(NH_2)_2$	233.1	254.7	262.0	235.2	241.4	256.4	230.4	235.3	234.7	249.4
$Mg(PH_2)_2$	186.5	175.1	201.0	172.9		212.8		188.3	184.3	188.1
$Mg^{+}(CH_3)_2$	215.4	257.2	256.0	244.7	254.5	252.5	248.7	219.2	215.3	227.0
mean error		10.8	14.9	8.1	13.3	13.6	6.0		0.3	1.0
mean absolute error		13.1	16.0	9.8	18.4	14.1	12.3		3.3	5.9
standard deviation		13.7	13.6	8.9	18.3	14.2	15.2		6.3	8.9
RMS error		17.4	20.1	12.0	22.6	19.6	16.3		6.3	9.0
no. of comparisons		20	20	20	16	20	16		20	20

[a] The SCC-DFTB parameters for Mg were fitted to reproduce B3LYP incremental binding energies.

All semiempirical methods underestimate the Mg−O and Mg−S bond lengths somewhat, and as mentioned before, various methods including SCC-DFTB predict bent rather than linear Mg−O−H structures. The energy differences associated with the various conformers are typically quite small, however, so that these failures depict minor shortcomings rather than intrinsically flawed methods. Both the MNDO and PM5 methods predict that compounds containing the Mg−P bonds such as Mg^+PH_2 and $Mg^{2+}(PH_3)_n$ ($n = 1-4$) will dissociate, whereas PM3 predicts stable molecules with bond lengths that are far too short. Only AM1 and SCC-DFTB predict qualitatively realistic scenarios, but of these AM1 overestimates the Mg−P bond lengths leaving SCC-DFTB as the only method to achieve quantitative accuracy.

B. Ionization Potentials. Ionization potentials are calculated for only four of the 75 compounds from the data set, there being experimental values available for these. The calculated results together with experimental ones are shown in Table 2. Not surprisingly, CBS provides excellent predictions, with mean and RMS errors from experiment of 0.01 and 0.11 eV, respectively, increasing to 0.15 and 0.34 eV for B3LYP/6-311++G**. SCC-DFTB underestimates the observed values by an average of 0.18 eV, whereas all other semiempirical methods overestimate them by an average of 0.21−0.39 eV; the RMS errors range from 0.42 to 0.65 eV, this maximum value being from PM3. SCC-DFTB here gives results of similar quality to the alternative fast computation methods.

C. Heats of Formation. The calculated heats of formation, along with any observed data, are listed in Supporting Information Table S2 for 59 molecules containing Mg and a further 16 molecules for which data are required for the subsequent determination of reaction energies; data obtained for an additional 12 magnesium-containing molecules with deprotonated ligands are not included, however, to limit bias of the statistical analyses. This statistical analysis of the results is presented in Table 3, grouped into Mg-containing and Mg-free compounds. First, experimental values of ΔH^f are compared to CBS values for the 17 molecules for which data are available. For the Mg-free compounds, an RMS error of 1.4 kcal mol^{-1} is obtained, comparable with results from extensive characterization of this method. [29] However, this increases to 5.0 kcal mol^{-1} for the Mg-containing species, due principally to large errors for $MgOH^+$ and magnesium diacetylacetonate ($Mg(acac)_2$, see Table S2); as the expected error in calculated heats of formation increases in proportion to the number of atoms in the molecule, this measure of computational accuracy is only useful when applied to small molecules. Subsequently, results for all other methods are compared to experiment, if available, and CBS-QB3 otherwise.

Optimized effective atomic heats of formation have been obtained by fitting the B3LYP and SCC-DFTB calculated data to reduce the RMS deviations from the reference data for Mg and for Mg and P, respectively, and the results are given in Table 4. Previously optimized values[49,50] are also included in this table for completeness. In general, the corrections to the heats of formation are expected to be dominated by the contribution that mimics zero-point energy, but for both B3LYP and SCC-DFTB the optimized corrections are negative for magnesium. This indicates that both methods struggle to reproduce the wide ranging chemistry (e.g., ionic bonding, covalent bonding, and dative bonding) available to magnesium. Further, the RMS error in the B3LYP calculations of the heat of formation of magnesium-containing compounds from Table 3 is 18 kcal mol^{-1}, many times larger than that generally expected for this method;[50] major errors are found for the large dicyclopentanyl and diacetylacetonate complexes only. Of all the methods considered, SCC-DFTB displays the largest errors, with a RMS error of 29 kcal mol^{-1} for magnesium-containing compounds. The smallest RMS error reported in Table 3 is 12 kcal mol^{-1} for PM5, but this result is distorted somewhat as six unbound phosphorus-containing complexes are not included

TABLE 6: Calculated Protonation Energies $-\Delta E^{H}$ (Eq 4), in kcal mol^{-1}, and the Statistical Comparison of Differences with the CBS Results

	with motional corrections									
		AM1						without corrections		
product	CBS-QB3	new	old	PM3	MNDO	MNDO/d	PM5	CBS-QB3	B3LYP	SCC-DFTB
$Mg^{2+}(H_2O)$	83.9	30.3	52.9	64.4	45.7	52.2	17.3	91.1	87.9	84.9
$Mg^{2+}(H_2O)_2$	104.2	55.1	68.9	81.5	74.2	70.9	40.0	111.3	87.0	107.7
$Mg^{2+}(H_2O)_3$	122.2	77.8	83.9	101.1	99.5	90.4	58.4	129.4	105.4	131.5
$Mg^{2+}(H_2O)_4$	138.3	92.1	93.9	114.9	120.1	107.7	72.9	145.6	121.3	150.6
$Mg^{2+}(SH_2)$	76.9	38.8	37.9	82.8	42.6	39.4	24.7	82.1	74.3	64.6
$Mg^{2+}(SH_2)_2$	99.0	58.0	55.9	92.8	64.5	63.0	41.6	104.3	78.7	87.8
$Mg^{2+}(SH_2)_3$	114.8	72.7	68.9	111.5	80.1	80.2	53.2	120.0	95.3	103.4
$Mg^{2+}(SH_2)_4$	126.7	77.6	77.9	122.3	92.4	93.2	59.9	132.0	107.8	116.4
$Mg^{2+}(NH_3)$	109.6	72.9	63.9	76.1	71.3	57.4	61.5	117.8	112.5	91.0
$Mg^{2+}(NH_3)_2$	133.8	95.5	81.9	99.7	96.5	78.6	85.2	142.0	116.3	114.6
$Mg^{2+}(NH_3)_3$	153.4	115.8	97.9	120.0	117.1	97.3	104.6	161.7	136.6	134.0
$Mg^{2+}(NH_3)_4$	169.4	134.7	120.9	143.0	138.2	116.2	123.0	179.3	154.5	156.6
$Mg^{2+}(PH_3)$	91.9	45.5	47.9	110.2		42.2		97.6	88.6	81.6
$Mg^{2+}(PH_3)_2$	122.8	67.7	71.9	145.7		68.8		128.7	102.0	110.2
$Mg^{2+}(PH_3)_3$	144.3	85.8	87.9	156.5		83.6		149.7	123.4	127.8
$Mg^{2+}(PH_3)_4$	158.3	100.0	96.9	164.6		96.7		164.4	138.0	140.8
mean error		−45.6	−46.3	−10.2	−32.5	−44.5	−57.5		−20.5	−15.8
mean absolute error		45.6	46.3	18.4	32.5	44.5	57.5		20.5	16.7
standard deviation		7.6	7.8	18.5	6.0	11.3	7.8		8.3	9.8
RMS error		46.2	46.9	21.1	33.0	45.9	58.0		22.1	18.6
no. of comparisons		16	16	16	12	16	12		16	16

in the analysis. The most significant errors found for SCC-DFTB are for MgO and magnesium hydroxides.

D. Incremental Binding Energies $-\Delta\Delta E$. Table 5 shows the incremental binding energies (see eq 3) for biological relevant ligands chelating the Mg^{2+} cation. Values obtained for B3LYP/6-311++G** and SCC-DFTB are compared to those obtained using CBS-QB3 with the motional corrections removed, whereas all other methods implicitly include thermal effects in their parametrizations and hence are compared to the full CBS-QB3 predictions.

The B3LYP calculations provide good results, with an RMS error compared to CBS-QB3 of just 6.3 kcal mol^{-1}. This error increases to just 9.0 kcal mol^{-1} for SCC-DFTB, indicating that the method is useful for the modeling of this biologically relevant process. For both B3LYP and SCC-DFTB, the ligation energies are predicted very much more accurately than are general heats of formation, indicating that dative chemical bonding is treated more reliably than are other motifs. Note, however, that these ligated compounds were used in the fitting of the SCC-DFTB repulsive potentials to B3LYP predictions and hence the results indicate the quality of the fit obtained rather than a priori predictions of chemical properties. For the other semiempirical methods, the RMS errors vary from 12 to 23 kcal mol^{-1}, of the order of those found for these methods evaluating general heats of formation of magnesium-containing compounds. These results indicate that the SCC-DFTB method is of particular merit for the study of the energetics of biologically relevant magnesium-containing molecules.

E. Protonation Energies $-\Delta E^{H}$. Table 6 shows the protonation energies calculated for 16 biological relevant ligand model molecules $Mg^{2+}(XH_m)_n$ ($X = N$, O, P, and S, $m = 2$ or 3 and $n = 1-4$) obtained using CBS-QB3, B3LYP/6-311++G**, and the semiempirical methods. Akin to the previous treatment of ligation energies, SCC-DFTB and B3LYP protonation energies are compared to the CBS-QB3 results with its thermal corrections removed and AM1, PM3, MNDO, MNDO/d, and PM5 results are compared to the full CBS-QB3 results.

The results obtained parallel those for the ligation energies in that the RMS errors for B3LYP and SCC-DFTB of 8.3 and 9.8 kcal mol^{-1}, respectively, are small enough to render these approaches useful, whereas the other semiempirical methods produce much larger RMS errors of 21−58 kcal mol^{-1}. The cause of this large error is not random scatter, however, as the mean errors reported in the table are of the same order as the RMS errors, and the standard deviations are quite low, just 6−13 kcal mol^{-1}. The large mean error arises from the difficulty of calculation of the energy of the H atom, a quantity that is compromised in most semiempirical methods to obtain improved accuracy for molecular properties.

4. Conclusions

Magnesium complexes are very important in biological systems, so an efficient and accurate quantum mechanism description of magnesium is an important goal. The computationally efficient SCC-DFTB method, as well as other semiempirical approximations including AM1, PM3, MNDO, MNDO/d and PM5 have been investigated and shown to be useful in many applications. Alternate less computationally efficient methods such as B3LYP (with a large basis set) and CBS-QB3 have also been investigated, with CBS-QB3 shown to provide results of very high quality and B3LYP approaching chemical accuracy for all properties except heats of formation. The SCC-DFTB method is found to predict realistic geometric properties, ionization potentials, incremental binding energies and protonation energies, generally significantly out performing the alternate semiempirical schemes, but is the least reliable method considered for heats of formation. Similar high-quality results for SCC-DFTB have also been found in general for small organic molecules, hydrogen-bonded complexes, DNA bases, Schiff bases, peptides, and fullerenes,[2−15] but the method is also known for its relatively poor heats of formation.[49] Poor performance for heats of formation stems from the overestimation of individual bond strengths by DFTB.[52]

More specifically, the calculation accuracy for the geometric properties for the semiempirical methods is found to be in the order SCC-DFTB > PM5, MNDO > AM1 > MNDO/d > PM3 for the bond lengths, and PM5 > AM1 > SCC-DFTB, MNDO, MNDO/d > PM3 for the bond angles. Qualitatively, PM3 predicts the highest number of incorrect molecular symmetries and bond conformations, and PM5 and AM1 predict the lowest number. SCC-DFTB performs in general quite well for predicting symmetry and conformation, the exception being Mg−O−H angles that are predicted to be bent instead of linear. For ionization energies, all of the semiempirical methods give similar performances, with SCC-DFTB predicting the least average error but one of the largest RMS errors. For heats of formation, PM5 appears to be the most accurate method but both it and MNDO fail to predict stable Mg−P bonds. AM1, PM3, and MNDO/d offer comparable accuracy, but SCC-DFTB results are quite poor. The failure of SCC-DFTB for heats of formation parallels the poor performance of B3LYP, the density functional used in parametrizing SCC-DFTB. The performance of SCC-DFTB for properties of direct biological relevance is significantly better than that for PM3, which is in turn significantly better than AM1, MNDO, MNDO/d and PM5.

Other questions of interest concern the performance of AM1 with its new[21] and old[20] paramererizations, and the relative performance of the older MNDO method, recently enhanced to include magnesium and some d-orbital atoms,[21] compared to the globally reparametrized MNDO/d method.[17] We find that the most significant difference between the AM1 parametrizations is that the new one predicts Mg−O−H conformations correctly quantitatively, it predicts slightly improved geometrical variables but slightly poorer heats of formation and ligation energies. The modified original MNDO method is poorer for conformations but slightly better for detailed geometries than is MNDO/d, but it fails in the case of phosphine ligands.

The excellent performance found for optimized geometries is particularly noteworthy as all of the empirical parameters used in the method act primarily to adjust the total energy and have minimal impact on optimized geometries. This result is in stark contrast to the other semiempirical schemes studied, as for these, geometrical data are explicitly used in the parametrization. Further, only a small number of incremental binding energies are used in the DFTB parametrization, so that SCC-DFTB is not optimized to reproduce absolute heats of formation, as are the alternate methods. Here, we see room for future improvement of SCC-DFTB by more extensive fitting to experimental data.

Magnesium offers considerable difficulties for all semiempirical methods as it can exist in a wide array of chemical bonding environments including ionic bonding, covalent bonding, and dative ligand bonding. The apparent hardness of the atom changes considerably in these environments, exposing inflexibilities in the parametric forms that limit variations in the atomic polarizability. We find for SCC-DFTB that the poorest results are obtained for interactions with oxygen anions, whereas bonds to phosphorus and sulfur are poorly described by most methods. Excellent results are obtained for SCC-DFTB for biologically relevant properties such as the geometries, ligation energies, and protonation energies of ligated complexes. The method should hence be very useful in biological applications. Improvements to DFTB involving a third-order expansion of DFT that includes chemical hardness variations are ensuing, however, and these are likely to significantly improve the method.[53]

Acknowledgment. We thank the Australian Research Council for funding this work and the Australian Partnership of Advanced Computing for the provision of computational resources. Financial support to M.E. by the Deutsche Forschungsgemeinschaft and the Fraunhofer-Gesellschaft is also gratefully acknowledged.

Supporting Information Available: Tables S1 and S2 describing in detail calculated and observed geometrical and energetic properties of the magnesium compounds and their components, as well as the complete version of ref 43. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Porezag, D.; Frauenheim, Th.; Koehler, Th.; Seifert, G.; Kaschner, R. *Phys. Rev. B* **1995**, *51*, 947.

(2) Elstner, M.; Porezag, D.; Jungnickel, G.; Elstner, J.; Haugk, M.; Frauenheim, T.; Suhai, S.; Seifert, G. *Phys. Rev. B* **1998**, *58*, 7620.

(3) Elstner, M.; Jalkanen, K. J.; Knapp-Mohammdy, M.; Frauenheim, T.; Suihai, S. *Phys. Stat. Solidi B* **2000**, *217*, 357.

(4) Elstner, M.; Cui, Q.; Munih, P.; Kaxiras, E.; Frauenheim, T.; Karplus, M. *J. Comput. Chem.* **2003**, *24*, 565.

(5) Bohr, H. G.; Jalkanen, K. J.; Elstner, M.; Frimand, K.; Suhai, S. *Chem. Phys.* **1999**, *246*, 13.

(6) Elstner, M.; Jalanen, K. J.; Knapp-Mohammady, M.; Frauenheim, T.; Suhai, S. *Chem. Phys.* **2000**, *256*, 15.

(7) Elstner, M.; Jalanen, K. J.; Knapp-Mohammady, M.; Frauenheim, T.; Suhai, S. *Chem. Phys.* **2001**, *263*, 203.

(8) Elstner, M.; Porezag, D.; Frauenheim, T.; Suhai, S.; Seifert, G. *MRS Symp. Proc.* **1999**.

(9) Krueger, T.; Elstner, M.; Schiffels, P.; Frauenheim, T. *J. Chem. Phys.* **2005**, *122*, 114110.

(10) Niehaus, T. A.; Elstner, M.; Frauenheim, T.; Suhai, S. *J. Mol. Struct. (THEOCHEM)* **2003**, *541*, 185.

(11) Shishkin, O. V.; Gorb, L.; Luzanov, A. V.; Elstner, M.; Suhai, S.; Leszczynski, J. *J. Mol. Struct. (THEOCHEM)* **2003**, *625*, 295.

(12) Zhou, H. Y.; Tajkhorshid, E.; Frauenheim, T.; Suhai, S.; Elstner, M. *Chem. Phys.* **2002**, *277*, 91.

(13) Abdali, S.; Niehaus, T. A.; Jalkanen, K. J.; Cao, X.; Nafie, L. A.; Frauenheim, T.; Suhai, S.; Bohr, H. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1295.

(14) Dolgonos, G.; Lukin, O.; Elstner, M.; Peslherbe, G. H.; Leszczynski, J. *J. Phys. Chem. A* **2006**, *110*, 9405.

(15) Elstner, M. *Theor. Chim. Acc.* **2006**, *116*, 316.

(16) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(17) Thiel, W.; Voityuk, A. A. *J. Phys. Chem.* **1996**, *100*, 616.

(18) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.

(19) Bredow, T.; Jug, K. *Theor. Chem. Acc.* **2005**, *113*, 1.

(20) Hutter, M. C.; Reimers, J. R.; Hush, N. S. *J. Phys. Chem. B* **1998**, *102*, 8080.

(21) Stewart, J. J. P. *J. Mol. Model.* **2004**, *10*, 155.

(22) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(23) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(24) Möller, C.; Plesset, M. S. *Phys. Rev. A* **1934**, *46*, 618.

(25) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(26) Petersson, G. A.; Al-Laham, M. A. *J. Chem. Phys.* **1991**, *94*, 6081.

(27) Petersson, G. A.; Tensfeldt, T. G.; Montgomery, J. A., Jr. *J. Chem. Phys.* **1991**, *94*, 6091.

(28) Montgomery, J. A., Jr.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1999**, *110*, 2822.

(29) Montgomery, J. A., Jr.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **2000**, *112*, 6532.

(30) Gardner, P. J.; Preston, S. R.; Siertsema, R.; Steele, D. J. *J. Comput. Chem.* **1993**, *14*, 1523.

(31) Taleb-Bendiab, A.; Chomiak, D. *Chem. Phys. Lett.* **2001**, *334*, 195.

(32) Milburn, R. K.; Bohme, D. K.; Hopkinson, A. C. *J. Mol. Struc. (THEOCHEM)* **2001**, *540*, 5.

(33) Magnusson, E. *J. Phys. Chem. A* **2001**, *105*, 3881.

(34) Merrill, G. N.; Webb, S. P.; Bivin, D. B. *J. Phys. Chem. A* **2003**, *107*, 386.

(35) Chen, Q.; Miburn, R. K.; Hopkinson, A. C.; Bohme, D. K.; Gooding, J. M. *Int. J. Mass Spectrosc.* **1999**, *184*, 153.

(36) Petrie, S. *J. Phys. Chem. A* **2002**, *106*, 7034.

(37) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure*; Van Nostrand: Princeton, NJ, 1979.

(38) Haaland, A.; Lusztyk, J.; Novak, D. P.; Brunvoll, J.; Strowieyski, K. B. *J. Chem. Soc., Chem. Commun.* **1974**, *54*.

(39) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(40) Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

(41) 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 B2; Gaussian, Inc.: Pittsburgh, PA, 2003.

(42) Rauhut, G.; Alex, A.; Chandrasekhar, J.; Steinke, T.; Sauer, W.; Beck, B.; Hutter, M.; Gedeck, P.; Clark, T. *VAMP Version 6.5*. Erlangen, 1997.

(43) Frisch, M. J.; Trucks, G. W.; Schlegel; et al. *GAUSSIAN 98*, revision A7; Gaussian Inc.: Pittsburgh, PA, 1998.

(44) Stewart, J. J. P. *MOPAC 2002*; Fujitsu Limited: Tokyo, 2002.

(45) Stewart, J. J. P. *J. Mol. Model.* **2004**, *10*, 6.

(46) Csonka, G. I.; Ruzinsky, A.; Tao, J.; Perdew, J. P. *Int. J. Quantum Chem.* **2005**, *101*, 506.

(47) Brothers, E. N.; Scuseria, G. E. *J. Chem. Theory Comput.* **2006**, *2*, 1045.

(48) Voityuk, A. A. *J. Chem. Theory Comput.* **2006**, *2*, 1038.

(49) Sattelmeyer, K. W.; Tirado-Rives, J.; Jorgensen, W. L. *J. Phys. Chem. A* **2006**, *110*, 13551−9.

(50) Winget, P.; Clark, T. *J. Comput. Chem.* **2004**, *25*, 725.

(51) Wiberg, K. B. *J. Comput. Chem.* **2003**, *25*, 1342.

(52) Otte, N.; Scholten, M.; Thiel, W. *J. Phys. Chem. A* **2007**, *111*, 5751.

(53) Elstner, M. *J. Phys. Chem. A* **2007**, *111*, 5614.

(54) Bauschlicher, C. W.; Sodupe, M.; Partridge, H. *J. Chem. Phys.* **1992**, *96*, 4453.

(55) Remko, M.; Rode, B. M. *J. Mol. Struct. (THEOCHEM)* **2000**, *505*, 269.

(56) Kerdcharoen, T.; Hannongbua, S. *Chem. Phys. Lett.* **1999**, *310*, 333.

(57) Nandi, P. K.; Sannigrahi, A. B. *J. Mol. Struct. (THEOCHEM)* **1994**, *307*, 99.

(58) Jalbout, A. F. *Chem. Phys. Lett.* **2001**, *340*, 571.

(59) Chase, M. W.; Davies, C. A.; Donney, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*.

(60) West, R. C. *CRC Handboook of Chemistry and Physics*, 60th ed.; CRC Press: Boca Raton, FL, 1974.

(61) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schum, R. H.; Halow, I.; Bailey, S. M.; Churmey, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*.

(62) Cox, J. O.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.

(63) Operti, L.; Tews, E. C.; MacMahon, T. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1989**, *111*, 9152.

(64) Lide, D. R. *CRC Handbook of Chemistry and Physics: A Ready-Reference Book of Chemical and Physical Data*; CRC Press Inc.: Boca Raton, FL, 1996.

(65) Gunn, S. R.; Green, L. R. *J. Phys. Chem.* **1961**, *65*, 779.

(66) Rice, A.; Bauschicher, C. W. *Chem. Phys. Lett.* **1998**, *285*, 455.

(67) Reynolds, C. H. *J. Org. Chem.* **1988**, *53*, 6061.

(68) Petrie, S.; Radom, L. *Int. J. Mass Spectrosc.* **1999**, *192*, 173.