

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231538426>

# Estimated Adiabatic Ionization Energies for Organic Compounds Using the Gaussian-4 (G4) and W1BD Theoretical Methods

ARTICLE in JOURNAL OF CHEMICAL & ENGINEERING DATA · DECEMBER 2010

Impact Factor: 2.04 · DOI: 10.1021/jc100913f

---

CITATIONS

10

---

READS

9

## 2 AUTHORS:



Sierra Rayne

Chemologica Research

270 PUBLICATIONS 2,282 CITATIONS

SEE PROFILE



Kaya Forest

Saskatchewan Polytechnic, Moose Jaw, Ca...

150 PUBLICATIONS 894 CITATIONS

SEE PROFILE

# Estimated Adiabatic Ionization Energies for Organic Compounds Using the Gaussian-4 (G4) and W1BD Theoretical Methods

Sierra Rayne<sup>\*,†</sup> and Kaya Forest<sup>‡</sup>

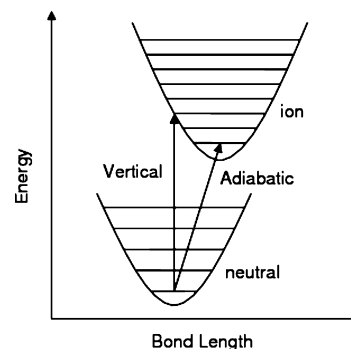
Ecologica Research, Kelowna, British Columbia, Canada V1Y 1R9, and Department of Chemistry, Okanagan College, Penticton, British Columbia, Canada V2A 8E1

Gas phase (298.15 K, 101.325 kPa) adiabatic ionization energies (AIEs) were calculated for 236 organic compounds with the Gaussian-4 (G4) composite method and for 17 molecules at the W1BD level of theory. Functional group types considered span a range of mono- and polyfunctionalized halogenated, saturated and unsaturated, cyclic and acyclic, and heteroatom (N, O, S) substituted moieties without substantial conformational complexity. Excellent agreement was found using both computational methods against available experimental data. Approximately equivalent AIE prediction accuracy was observed between the G4 and the W1BD methods. For compounds with well-constrained experimental AIEs, both levels of theory provide effective chemical accuracy.

## Introduction

The ionization energy (IE) represents the minimum energy to eject an electron from a neutral molecule in its ground state. Two types of IEs are defined. The adiabatic ionization energy (AIE) involves the formation of the resulting molecular ion in its ground vibrational state following electron ejection, a process which allows for geometrical rearrangement in the overall energy change (Figure 1). In contrast, the vertical ionization energy (VIE) does not allow for geometrical rearrangements upon molecular ion formation and strictly involves electron ejection with a stationary geometry.<sup>1</sup> AIEs are not only of interest from a theoretical perspective in terms of defining molecular properties such as electronegativity and chemical potential, hardness/softness, and the electrophilicity index and for broadly understanding structure–reactivity relationships,<sup>2–7</sup> but they are also widely employed toward redox processes in natural, engineered, and biological systems and in the design of new materials.<sup>8–11</sup>

Because of interest in the redox properties of larger supramolecular systems and biologically relevant macromolecules, the majority of theoretical IE benchmarking efforts have been performed using density functional and Hartree–Fock levels of theory (see, e.g., refs 12 to 17), both of whose computational costs scale favorably with molecular size compared to higher level composite methods. More restricted benchmarking studies in terms of molecular size and number of compounds have been conducted using the earlier Gaussian-1 (G1) through G3 versions of the higher level Gaussian-*n* methods and W1/W2 theory.<sup>18–21</sup> To date, the G4 method has been benchmarked against 105 compounds from the G3/05 test set, where a mean absolute deviation (MAD) and a root-mean-squared deviation (rmsd) of (0.04 and 0.06) eV were obtained, respectively.<sup>22</sup> The W1BD (along with the W1U, W1Usc, and W1(RO) flavors of W1 theory) method has been similarly benchmarked against 86 compounds from the G2/97 test set, yielding MAD and rmsd of 0.02 eV.<sup>23</sup>



**Figure 1.** Schematic potential energy diagram for a diatomic molecule illustrating the difference between adiabatic and vertical ionization energies. Adapted from <http://cccbdb.nist.gov/adiabatic.asp>.

There remains much interest in molecular systems amenable to composite method calculations, and with continuing increases in computing power and the development of more efficient algorithms, we expect increasingly larger molecules will be within reach of these calculations in the near future. The current work extends AIE benchmarking efforts with the G4 and W1BD methods to a larger suite of functionalized organic compounds of varying molecular size and also provides high level AIE estimates for a number of well-known strained organic compounds whose properties are of fundamental and applied importance.

## Methodology

Compound structures and experimental data were obtained from the National Institute of Standards and Technology (NIST) Chemistry WebBook.<sup>24</sup> Where applicable, two-dimensional structures from this reference database were converted to three-dimensional geometries using Avogadro v.1.0.1. All compounds were subjected to a systematic rotor search which identified the lowest energy MMFF94s<sup>25–29</sup> conformation followed by a 500 step geometry optimization using the steepest descent algorithm and a convergence criterion of  $10^{-7}$  within the Avogadro software environment. The resulting geometries were used as

\* Corresponding author. E-mail: rayne.sierra@gmail.com.

<sup>†</sup> Ecologica Research.

<sup>‡</sup> Okanagan College.

**Table 1.** Experimental and G4/W1BD Calculated Gas Phase (298.15 K, 101.325 kPa) AIEs for Various Small Organic Compounds<sup>a</sup>

CAS-RN	formula	MW	name	AIE/eV		
		g·mol <sup>-1</sup>		expt.	G4	W1BD
74-86-2	C <sub>2</sub> H <sub>2</sub>	26.0373	acetylene	11.400 ± 0.002	11.41	11.40
74-90-8	CHN	27.0253	hydrogen cyanide	13.60 ± 0.01	13.61	13.62
630-08-0	CO	28.0101	carbon monoxide	14.014 ± 0.0003	14.05	14.04
50-00-0	CH <sub>2</sub> O	30.0260	formaldehyde	10.88 ± 0.01	10.89	10.91
74-89-5	CH <sub>5</sub> N	31.0571	methylamine	8.9 ± 0.1	9.05	9.06
115-07-1	C <sub>3</sub> H <sub>6</sub>	42.0797	propene	9.73 ± 0.01	9.77	9.76
124-38-9	CO <sub>2</sub>	44.0095	carbon dioxide	13.777 ± 0.001	13.78	13.84
75-21-8	C <sub>2</sub> H <sub>4</sub> O	44.0526	ethylene oxide	10.56 ± 0.01	10.58	10.60
75-07-0	C <sub>2</sub> H <sub>4</sub> O	44.0526	acetaldehyde	10.2290 ± 0.0007	10.23	10.26
64-18-6	CH <sub>2</sub> O <sub>2</sub>	46.0254	formic acid	11.33 ± 0.01	11.30	11.35
75-02-5	C <sub>2</sub> H <sub>3</sub> F	46.0436	fluoroethene	10.36 ± 0.01	10.35	10.37
74-93-1	CH <sub>4</sub> S	48.107	methanethiol	9.439 ± 0.005	9.45	9.45
74-87-3	CH <sub>3</sub> Cl	50.488	chloromethane	11.26 ± 0.03	11.26	11.30
75-10-5	CH <sub>2</sub> F <sub>2</sub>	52.0234	difluoromethane	12.71	12.76	12.77
506-77-4	CClN	61.470	cyanogen chloride	12.36 ± 0.02	12.33	12.41
75-01-4	C <sub>2</sub> H <sub>3</sub> Cl	62.498	chloroethene	9.99 ± 0.02	9.98	10.02
353-50-4	CF <sub>2</sub> O	66.0069	carbonic difluoride	13.04 ± 0.03	12.96	13.04

<sup>a</sup> Experimental values are the evaluated AIEs taken from the compendium of Lias<sup>52</sup> in the NIST Database.

inputs for Gaussian-4 (G4)<sup>22</sup> and W1BD<sup>23,30</sup> composite method calculations with Gaussian 09.<sup>31</sup>

All molecular enthalpies and free energies include zero-point, thermal, and composite method specific corrections. No compounds have imaginary frequencies at the final optimized geometry. Only the lowest energy conformation of each compound was considered. Gabedit v.2.2.12 was used for geometry visualization.<sup>32</sup> Optimized geometries, energies at each step of the calculation process, and frequency coordinates for the cationic forms of all compounds are provided in the Supporting Information. The neutral forms of all compounds were calculated at the G4 and W1BD levels of theory as part of our previous work.<sup>33</sup> The cationic forms of all compounds from ref 33 were examined as part of the current investigation. Cationic structures which failed to converge or yielded imaginary frequencies were not considered further, giving the reduced set of compounds presented herein. Structures and Gaussian 09 archive entries for the neutral forms can be obtained from this prior reference. Molecular enthalpies and free energies for all neutral and cationic forms at both levels of theory are given in the Supporting Information.

## Results and Discussion

Gas phase (298.15 K, 101.325 kPa) AIEs were initially calculated at the G4 and W1BD levels of theory for 17 organic compounds having well-constrained NIST evaluated experimental AIEs (Table 1). A wide range of functional groups were examined, including saturated and unsaturated, cyclic and acyclic, halogenated, thiol, amine, alcohol, aldehyde, carboxylic acid, ether, and cyano moieties. Excellent agreement between the theoretical and the experimental AIEs was observed. The mean signed deviation (MSD), mean absolute deviation (MAD), and root-mean-squared deviation (rmsd) of (0.01, 0.03, and 0.05) eV, respectively, were obtained for the G4 method against the experimental data. Corresponding MSD, MAD, and rmsd values of (0.04, 0.04, and 0.05) eV, respectively, were obtained for the W1BD method against the experimental data. The maximum absolute individual deviations were (0.15 and 0.16) eV for the G4 and W1BD methods, respectively. MAD and rmsd of (0.03 and 0.04) eV, respectively, were obtained between the G4 and the W1BD methods.

The excellent agreement in AIE estimation capability between the G4 and the W1BD levels of theory and against high quality experimental data, coupled with the substantial computational

cost of the W1BD method for larger compounds, led us to use only the G4 method to examine the AIEs for a broader suite of 134 organic compounds having experimental AIE data of varying quality (Table 2). Excellent agreement between the G4 and the experimental AIEs was obtained, particularly where NIST evaluated experimental values were available. For the 56 compounds having NIST evaluated AIEs, the MSD, MAD, and rmsd of (−0.02, 0.06, and 0.09) eV, respectively, were obtained between the G4 and the experimental values, with a maximum absolute individual deviation of 0.30 eV (isopentane).

In some cases, the G4 values may assist in obtaining an evaluated AIE or in the reassessment of an evaluated AIE. For example, the evaluated AIE for isopentane is 10.32 ± 0.05 eV, and experimental data for this compound range between (10.18<sup>34</sup> and 10.50 ± 0.05) eV.<sup>35</sup> Given the known wide variability in measuring AIEs for saturated hydrocarbons, particularly where rapid postionization carbocation isomerization can occur, the true AIE for isopentane may be closer to the G4 estimate of 10.02 eV. Similarly, some compounds have evaluated AIEs with large error bars (e.g. chlorotrifluoromethane, 12.6 ± 0.4 eV; difluorodichloromethane, 12.0 ± 0.2 eV); in these cases, the G4 estimates are either within (chlorotrifluoromethane, 12.42 eV) or near (difluorodichloromethane, 11.73 eV) the error boundaries and may help in better constraining the actual AIEs for these molecules.

For a number of common organic compounds, the experimental AIEs span a surprisingly large range, attesting to the difficulty in reliable experimental determinations. Thus, high level computational estimates may resolve residual experimental uncertainty. Dimethyl sulfoxide has experimental AIE reports of 9.9 ± 0.1 eV,<sup>36</sup> 9.20 ± 0.05 eV,<sup>37</sup> 9.08 ± 0.09 eV,<sup>38</sup> and 9.10 eV.<sup>39</sup> The G4 estimate of 8.86 eV suggests that the experimental value of 9.9 ± 0.1 is likely an outlier and that the true value is either near ~9.1 eV or potentially lower. Pyrazine has experimental AIE values of 9.29 ± 0.03 eV,<sup>40</sup> 9.29 ± 0.01 eV,<sup>41</sup> 9.36 eV,<sup>42</sup> 9.28 ± 0.05 eV,<sup>43</sup> 9.216 eV,<sup>44</sup> 9.29 eV,<sup>45</sup> 9.28 ± 0.01 eV,<sup>46</sup> and 9.0 eV.<sup>47</sup> The G4 estimate of 9.28 eV is in excellent agreement with the majority of experimental reports and suggests the proposed experimental values of (9.36 and 9.0) eV are likely high and low outliers, respectively. An evaluated AIE for this compound can likely be put forward as 9.28 ± 0.01 eV. As a final illustration, azetidine has experimental AIEs of 9.1 ± 0.15 eV,<sup>48</sup> 8.9 eV,<sup>49</sup> 8.3 eV,<sup>50</sup> and 8.63 ± 0.02 eV<sup>51</sup> that span 0.8 eV. The G4 prediction of 8.32 eV is at the lower

Table 2. Experimental and G4 Calculated Gas Phase (298.15 K, 101.325 kPa) AIEs for Various Organic Compounds<sup>a</sup>

CAS-RN	formula	MW		name	AIE/eV		formula	MW		name	AIE/eV	
		g·mol <sup>-1</sup>	g·mol <sup>-1</sup>		expt	expt		g·mol <sup>-1</sup>	g·mol <sup>-1</sup>		expt	expt
689-97-4	C <sub>4</sub> H <sub>4</sub>	52.0746	52.0746	1-buten-3-yne	9.58 ± 0.02		C <sub>6</sub> H <sub>14</sub>	86.1754	86.1754	hexane	10.13 ± 0.10	10.00
2873-50-9	C <sub>4</sub> H <sub>4</sub>	52.0746	52.0746	1,2,3-butatriene	9.15 to 9.40		C <sub>7</sub> H <sub>6</sub>	90.1225	90.1225	1,1-diethynylcyclopropane	8.9	8.95
1120-53-2	C <sub>4</sub> H <sub>4</sub>	52.0746	52.0746	cyclobutadiene	8.16 to 9.55		C <sub>7</sub> H <sub>6</sub>	90.1225	90.1225	5-ethynylidene-1,3-cyclopentadiene	8.88	8.23
107-13-1	C <sub>3</sub> H <sub>3</sub> N	53.0626	53.0626	2-propenenitrile	10.91 ± 0.01		C <sub>7</sub> H <sub>6</sub>	90.1225	90.1225	cis-1,2-diethynylcyclopropane	8.90	8.92
157-33-5	C <sub>4</sub> H <sub>6</sub>	54.0904	54.0904	bicyclo[1.1.0]butane	8.70 ± 0.01		C <sub>7</sub> H <sub>6</sub>	90.1225	90.1225	trans-1,2-diethynylcyclopropane	9.00	8.89
822-35-5	C <sub>4</sub> H <sub>6</sub>	54.0904	54.0904	cyclobutene	9.43 ± 0.02		C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	92.0987	92.0987	pyrrole-2-carbonitrile	8.7	8.86
6788-85-8	C <sub>3</sub> H <sub>3</sub> N	55.0785	55.0785	1-azetene	9.30		C <sub>7</sub> H <sub>8</sub>	92.1384	92.1384	2,5-norbornadiene	8.38 ± 0.04	8.39
115-11-7	C <sub>4</sub> H <sub>8</sub>	56.1063	56.1063	2-methyl-1-propene	9.22 ± 0.02		C <sub>7</sub> H <sub>8</sub>	92.1384	92.1384	3-methylene-1,4-cyclohexadiene	8.6	8.12
590-18-1	C <sub>4</sub> H <sub>8</sub>	56.1063	56.1063	cis-2-butene	9.11 ± 0.01		C <sub>7</sub> H <sub>8</sub>	92.1384	92.1384	5-methylenebicyclo[2.2.0]hex-2-ene	8.8	8.80
624-64-6	C <sub>4</sub> H <sub>8</sub>	56.1063	56.1063	trans-2-butene	9.10 ± 0.01		C <sub>7</sub> H <sub>8</sub>	92.1384	92.1384	bicyclo[3.2.0]hepta-2,6-diene	8.35	8.68
1072-44-2	C <sub>3</sub> H <sub>7</sub> N	57.0944	57.0944	1-methylaziridine	8.7		C <sub>7</sub> H <sub>8</sub>	92.1384	92.1384	quadricyclane	7.80 to 8.70	7.66
503-29-7	C <sub>3</sub> H <sub>7</sub> N	57.0944	57.0944	azetidine	8.3 to 9.1		C <sub>7</sub> H <sub>8</sub>	92.1384	92.1384	spiro[2.4]hepta-4,6-diene	8.14	8.11
75-56-9	C <sub>3</sub> H <sub>6</sub> O	58.0791	58.0791	methyloxirane	10.22 ± 0.02		C <sub>7</sub> H <sub>8</sub>	92.1384	92.1384	spiro[3.3]hepta-2,5-diene	9.02	9.01
503-30-0	C <sub>3</sub> H <sub>6</sub> O	58.0791	58.0791	oxetane	9.65 ± 0.01		C <sub>7</sub> H <sub>8</sub>	92.1384	92.1384	toluene	8.828 ± 0.001	8.86
75-56-9	C <sub>3</sub> H <sub>6</sub> O	58.0791	58.0791	propylene oxide	10.22 ± 0.02		C <sub>6</sub> H <sub>7</sub> N	93.1265	93.1265	2-methylpyridine	9.02 to 9.40	9.01
64-19-7	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	60.0520	60.0520	acetic acid	10.65 ± 0.02		C <sub>6</sub> H <sub>7</sub> N	93.1265	93.1265	aniline	7.720 ± 0.002	7.74
75-38-7	C <sub>2</sub> H <sub>3</sub> F <sub>2</sub>	64.0341	64.0341	1,1-difluoroethene	10.29 ± 0.0		C <sub>6</sub> H <sub>6</sub> O	94.1112	94.1112	phenol	8.49 ± 0.02	8.53
21986-03-8	C <sub>3</sub> H <sub>4</sub>	64.0853	64.0853	1,2,3,4-pentatetraene	8.67		C <sub>6</sub> H <sub>10</sub>	94.1543	94.1543	1-methyl-1,2-propadienylcyclopropane	8.83	8.28
24442-69-1	C <sub>3</sub> H <sub>4</sub>	64.0853	64.0853	penta-1,4-diene	10.10 to 10.27		C <sub>7</sub> H <sub>10</sub>	94.1543	94.1543	2-norbornene	8.60 to 9.05	8.80
1574-40-9	C <sub>3</sub> H <sub>6</sub>	66.1011	66.1011	(Z)-3-penten-1-yne	9.11		C <sub>7</sub> H <sub>10</sub>	94.1543	94.1543	5,5-dimethyl-1,3-cyclopentadiene	8.20 to 8.22	8.35
646-05-9	C <sub>3</sub> H <sub>6</sub>	66.1011	66.1011	1-penten-3-yne	9.00 ± 0.01		C <sub>7</sub> H <sub>10</sub>	94.1543	94.1543	tricyclo[3.1.1.0 <sup>3,6</sup> ]heptane	8.7	8.71
542-92-7	C <sub>3</sub> H <sub>6</sub>	66.1011	66.1011	1,3-cyclopentadiene	8.57 ± 0.01		C <sub>7</sub> H <sub>10</sub>	94.1543	94.1543	tricyclo[4.1.0.0 <sup>1,3</sup> ]heptane	8.6	8.54
78-80-8	C <sub>3</sub> H <sub>6</sub>	66.1011	66.1011	2-methyl-1-buten-3-yne	9.25 ± 0.02		C <sub>4</sub> H <sub>5</sub> N <sub>3</sub>	95.1026	95.1026	3-methyl-1,2,4-triazine	8.6	8.77
5164-35-2	C <sub>3</sub> H <sub>6</sub>	66.1011	66.1011	bicyclo[2.1.0]pent-2-ene	8.0		C <sub>3</sub> H <sub>8</sub> N <sub>2</sub>	96.1304	96.1304	2,3-diazabicyclo[2.2.1]-hept-2-ene	8.45	8.54
6746-94-7	C <sub>3</sub> H <sub>6</sub>	66.1011	66.1011	cyclopropylacetylene	8.7		C <sub>2</sub> H <sub>3</sub> Cl <sub>2</sub>	96.943	96.943	1,1-dichloroethene	9.81 ± 0.04	9.78
109-97-7	C <sub>4</sub> H <sub>3</sub> N	67.0892	67.0892	pyrrole	8.207 ± 0.005		C <sub>2</sub> H <sub>3</sub> Cl <sub>2</sub>	96.943	96.943	cis-1,2-dichloroethene	9.66 ± 0.01	9.61
504-64-3	C <sub>3</sub> O <sub>2</sub>	68.0309	68.0309	carbon suboxide	10.60		C <sub>2</sub> H <sub>3</sub> Cl <sub>2</sub>	96.943	96.943	trans-1,2-dichloroethene	9.64 ± 0.02	9.57
110-00-9	C <sub>4</sub> H <sub>4</sub> O	68.0740	68.0740	furan	8.88 ± 0.01		CCl <sub>3</sub> O	98.916	98.916	phosgene	11.2 to 11.7	11.50
288-32-4	C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	68.0773	68.0773	1H-imidazole	8.81 ± 0.01		C <sub>2</sub> F <sub>4</sub>	100.0150	100.0150	tetrafluoroethene	10.14 ± 0.07	10.05
288-13-1	C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	68.0773	68.0773	1H-pyrazole	9.25 to 9.38		C <sub>8</sub> H <sub>6</sub>	102.1332	102.1332	bicyclo[4.2.0]octa-1,3,5,7-tetraene	7.5	7.76
185-94-4	C <sub>3</sub> H <sub>8</sub>	68.1170	68.1170	bicyclo[2.1.0]pentane	8.7		C <sub>8</sub> H <sub>6</sub>	102.1332	102.1332	phenylacetylene	8.81 to 8.90	8.84
157-40-4	C <sub>3</sub> H <sub>8</sub>	68.1170	68.1170	spiropentane	9.26		C <sub>8</sub> H <sub>6</sub>	104.1491	104.1491	(1 $\alpha$ ,2 $\beta$ ,5 $\beta$ ,6 $\alpha$ )-tricyclo[4.2.0.0 <sup>2,5</sup> ]octa-3,7-diene	8.27	8.68
109-96-6	C <sub>4</sub> H <sub>7</sub> N	69.1051	69.1051	2,5-dihydro-1H-pyrrole	8.0		C <sub>8</sub> H <sub>8</sub>	104.1491	104.1491	1,5-dihydro-pentalene	7.86	7.86
75-46-7	CHF <sub>3</sub>	70.0138	70.0138	trifluoromethane	13.86		C <sub>8</sub> H <sub>8</sub>	104.1491	104.1491	7-methylenebicyclo[2.2.1]hepta-2,5-diene	8.5	8.41
1467-79-4	C <sub>3</sub> H <sub>6</sub> N <sub>2</sub>	70.0931	70.0931	dimethylcyanamide	9.0		C <sub>8</sub> H <sub>8</sub>	104.1491	104.1491	bicyclo[2.2.2]octa-2,5,7-triene	7.95 to 8.24	8.23
109-99-9	C <sub>4</sub> H <sub>8</sub> O	72.1057	72.1057	tetrahydrofuran	10.32 ± 0.02		C <sub>8</sub> H <sub>8</sub>	104.1491	104.1491	bicyclo[4.2.0]octa-1,3,5-triene	8.74	8.67
78-49-4	C <sub>5</sub> H <sub>12</sub>	72.1488	72.1488	isopentane	9.42 ± 0.05		C <sub>8</sub> H <sub>8</sub>	104.1491	104.1491	cycloocta-1,3-dien-6-yne	8.5	8.60
463-82-1	C <sub>5</sub> H <sub>12</sub>	72.1488	72.1488	neopentane	≤10.30 ± 0.08		C <sub>8</sub> H <sub>8</sub>	104.1491	104.1491	cycloocta-1,5-dien-3-yne	8.2	8.37
109-66-0	C <sub>5</sub> H <sub>12</sub>	72.1488	72.1488	pentane	10.28 ± 0.10		C <sub>8</sub> H <sub>8</sub>	104.1491	104.1491	pentacyclo[3.3.0.0 <sup>2,4</sup> .0 <sup>3,7</sup> .0 <sup>6,8</sup> ]octane	8.18	8.25
1071-98-3	C <sub>4</sub> N <sub>2</sub>	76.0562	76.0562	2-butyne	11.40 to 11.81		C <sub>8</sub> H <sub>8</sub>	104.1491	104.1491	styrene	8.464 ± 0.001	8.49
16668-68-1	C <sub>6</sub> H <sub>4</sub>	76.0960	76.0960	(E)-hexa-1,5-diene-3-yne	9.07		C <sub>8</sub> H <sub>8</sub>	104.1491	104.1491	tetrakis(methylene)cyclobutane	8.35	8.35
16668-67-0	C <sub>6</sub> H <sub>4</sub>	76.0960	76.0960	(Z)-hexa-1,5-diene-3-yne	9.10		C <sub>8</sub> H <sub>8</sub>	104.1491	104.1491	tricyclo[4.1.1.0 <sup>7,8</sup> ]octa-2,4-diene	7.9	8.07
6929-94-8	C <sub>6</sub> H <sub>4</sub>	76.0960	76.0960	hex-3-en-1,5-diene	9.6		C <sub>8</sub> H <sub>8</sub>	104.1491	104.1491	chlorotrifluoromethane	12.6 ± 0.4	12.42
75-15-0	CS <sub>2</sub>	76.141	76.141	carbon disulfide	10.073 ± 0.005		CClF <sub>3</sub>	104.459	104.459	1,5-dimethyl-3-exomethylenetricyclo[2.1.0.0]pentane	8.0	7.65
5291-90-7	C <sub>6</sub> H <sub>6</sub>	78.1118	78.1118	3,4-dimethylenecyclobut-1-ene	8.80		C <sub>8</sub> H <sub>10</sub>	106.1650	106.1650	bicyclo[3.2.1]octa-2,6-diene	8.44	8.32
71-43-2	C <sub>6</sub> H <sub>6</sub>	78.1118	78.1118	benzene	9.24378 ± 0.00007		C <sub>8</sub> H <sub>10</sub>	106.1650	106.1650	bicyclo[4.1.1.0 <sup>7,8</sup> ]oct-2-ene	8.2	8.24
5649-95-6	C <sub>6</sub> H <sub>6</sub>	78.1118	78.1118	bicyclo[2.2.0]hexa-2,5-diene	9.0		C <sub>8</sub> H <sub>10</sub>	106.1650	106.1650	tricyclo[4.1.1.0 <sup>7,8</sup> ]oct-3-ene	9.07 ± 0.02	9.09
3227-90-5	C <sub>6</sub> H <sub>6</sub>	78.1118	78.1118	tris(methylene)cyclopropane	9.0		C <sub>8</sub> H <sub>10</sub>	112.557	112.557	chlorobenzene	9.33 ± 0.02	9.34
67-68-5	C <sub>2</sub> H <sub>6</sub> OS	78.133	78.133	dimethyl sulfoxide	9.08 to 9.90		C <sub>6</sub> H <sub>5</sub> Cl	114.0928	114.0928	<i>m</i> -difluorobenzene	9.29 ± 0.01	9.30
290-37-9	C <sub>4</sub> H <sub>4</sub> N <sub>2</sub>	80.0880	80.0880	pyrazine	9.00 to 9.36		C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	114.0928	114.0928	<i>o</i> -difluorobenzene	9.1589 ± 0.0005	9.15
289-80-5	C <sub>4</sub> H <sub>4</sub> N <sub>2</sub>	80.0880	80.0880	pyridazine	8.74 ± 0.11		C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	114.0928	114.0928	<i>p</i> -difluorobenzene		
289-95-2	C <sub>4</sub> H <sub>4</sub> N <sub>2</sub>	80.0880	80.0880	pyrimidine	9.33 ± 0.07		C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	114.0928	114.0928			

Table 2. Continued

CAS-RN	formula	MW g·mol <sup>-1</sup>	name	AIE/eV		MW g·mol <sup>-1</sup>	name	AIE/eV	
				expt	G4			expt	G4
96-39-9	C <sub>6</sub> H <sub>8</sub>	80.1277	1-methyl-1,3-cyclopentadiene	8.40 ± 0.02	8.16	673-32-5	C <sub>9</sub> H <sub>8</sub>	8.42	8.43
2045-78-5	C <sub>6</sub> H <sub>8</sub>	80.1277	1,3-bis(methylene)cyclobutane	8.7	9.11	79-38-9	C <sub>2</sub> ClF <sub>3</sub>	9.81 ± 0.03	9.76
930-26-7	C <sub>6</sub> H <sub>8</sub>	80.1277	3-methylenecyclopentene	8.40	8.32	67-66-3	CHCl <sub>3</sub>	11.37 ± 0.02	11.42
96-38-8	C <sub>6</sub> H <sub>8</sub>	80.1277	5-methyl-1,3-cyclopentadiene	8.45	8.47	75-71-8	CCl <sub>2</sub> F <sub>2</sub>	12.0 ± 0.2	11.73
3097-63-0	C <sub>6</sub> H <sub>8</sub>	80.1277	bicyclo[2.2.0]hex-2-ene	9.0	8.90	79-01-6	C <sub>2</sub> HCl <sub>3</sub>	9.46 ± 0.02	9.41
290-38-0	C <sub>3</sub> H <sub>3</sub> N <sub>3</sub>	81.0760	1,2,4-triazine	9.2	9.08	83589-40-6	CCl <sub>3</sub> F	11.68 ± 0.13	11.69
78104-88-8	C <sub>3</sub> H <sub>7</sub> N	81.1158	1-methylcyclopropanecarbonitrile	10.53	9.92	81044-78-2	C <sub>6</sub> H <sub>4</sub> S <sub>2</sub>	8.15	8.32
359-11-5	C <sub>3</sub> HF <sub>3</sub>	82.0245	trifluoroethene	10.14	10.10	251-41-2	C <sub>6</sub> H <sub>4</sub> S <sub>2</sub>	8.10	8.11
420-46-2	C <sub>3</sub> H <sub>4</sub> F <sub>3</sub>	84.0404	1,1,1-trifluoroethane	13.3	12.48	541-73-1	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	9.10 ± 0.02	9.13
290-67-5	C <sub>3</sub> H <sub>4</sub> O <sub>2</sub>	84.0734	1,4-dioxin	7.75	7.85	95-50-1	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	9.06 ± 0.02	9.05
674-82-8	C <sub>3</sub> H <sub>4</sub> O <sub>2</sub>	84.0734	4-methylene-2-oxetanone	9.6	9.34	106-46-7	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	8.92 ± 0.03	8.91
674-82-8	C <sub>3</sub> H <sub>4</sub> O <sub>2</sub>	84.0734	diketene	9.6	9.34	75-87-6	C <sub>2</sub> HC <sub>3</sub> O	10.9	10.36
110-02-1	C <sub>3</sub> H <sub>4</sub> S	84.140	thiophene	8.86 ± 0.02	8.89	56-23-5	CCl <sub>4</sub>	11.47 ± 0.01	11.53
75-09-2	CH <sub>2</sub> Cl <sub>2</sub>	84.933	dichloromethane	11.33 ± 0.04	11.10	127-18-4	C <sub>2</sub> Cl <sub>4</sub>	9.326 ± 0.001	9.24
1708-32-3	C <sub>3</sub> H <sub>6</sub> S	86.155	2,5-dithiophene	8.4	8.49	120-82-1	C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub>	9.04 ± 0.03	8.97

<sup>a</sup> Single experimental values are either the evaluated AIEs taken from the compendia of Lias<sup>52</sup> and Lias et al.<sup>53</sup> in the NIST Database or are single non-evaluated experimental data points. All other experimental values are the lower and upper boundaries of multiple individual data points. Experimental data taken from ref 54 with full referencing for all individual data points provided in the Supporting Information.

Table 3. G4 Calculated Gas Phase (298.15 K, 101.325 kPa) AIEs for Various Organic Compounds Which Lack Experimental AIE Data

CAS-RN	formula	MW g·mol <sup>-1</sup>	compound	G4 AIE		MW g·mol <sup>-1</sup>	formula	compound	G4 AIE	
				eV	CAS-RN				eV	CAS-RN
4095-06-1	C <sub>3</sub> H <sub>4</sub>	52.0746	methylenecyclopropane	8.13	3839-50-7	C <sub>3</sub> H <sub>8</sub>	92.1384	6-methylfulvene	8.10	8.10
58208-49-4	C <sub>3</sub> H <sub>4</sub>	52.0746	bicyclo[1.1.0]but-1(3)-ene	9.16	31357-71-8	C <sub>2</sub> H <sub>7</sub> N	93.1265	bicyclo[2.1.0]pentane-1-carbonitrile	9.26	9.26
3100-04-7	C <sub>3</sub> H <sub>6</sub>	54.0904	1-methylcyclopropane	9.11	287-13-8	C <sub>3</sub> H <sub>10</sub>	94.1543	tricyclo[4.1.0.0 <sup>2,7</sup> ]heptane	8.35	8.35
54376-32-8	C <sub>3</sub> H <sub>5</sub> N	55.0785	cyclopropanimine	8.80	187-26-8	C <sub>3</sub> H <sub>10</sub>	94.1543	tricyclo[4.1.0.0 <sup>2,4</sup> ]heptane	8.80	8.80
59078-44-3	C <sub>3</sub> H <sub>4</sub> O	68.0740	cyclopropylidenemethanone	8.75	87304-84-5	C <sub>3</sub> H <sub>10</sub>	94.1543	<i>syn</i> -tricyclo[3.2.0.0 <sup>2,4</sup> ]heptane	8.04	8.04
33898-53-2	C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	68.0773	2-aziridinecarbonitrile	10.22	121733-05-9	C <sub>3</sub> H <sub>10</sub>	94.1543	<i>endo</i> -2-methylene-5-methylbicyclo[2.1.0]pentane	8.04	8.04
18631-84-0	C <sub>3</sub> H <sub>8</sub>	68.1170	methylmethylenecyclopropane	9.22	54140-30-6	C <sub>3</sub> H <sub>10</sub>	94.1543	cyclopentyl acetylene	9.66	9.66
18631-83-9	C <sub>3</sub> H <sub>8</sub>	68.1170	ethylidenecyclopropane	9.02	10563-10-7	C <sub>3</sub> H <sub>10</sub>	94.1543	bicyclo[3.2.0]hept-1(5)-ene	8.40	8.40
14309-32-1	C <sub>3</sub> H <sub>8</sub>	68.1170	1,2-dimethylcyclopropane	8.60	22630-75-7	C <sub>3</sub> H <sub>10</sub>	94.1543	bicyclo[3.2.0]hept-1(5)-ene	8.33	8.33
1489-60-7	C <sub>3</sub> H <sub>8</sub>	68.1170	1-methylcyclobutene	8.92	28102-61-6	C <sub>3</sub> H <sub>10</sub>	94.1543	antitricyclo[3.2.0.0 <sup>2,4</sup> ]heptane	8.48	8.48
n/a	C <sub>3</sub> H <sub>6</sub> O	70.0898	3-methylenecyclohexane	9.49	74503-34-7	C <sub>3</sub> H <sub>10</sub>	94.1543	5,5-dimethylbicyclo[2.1.0]pent-2-ene	7.87	7.87
1708-29-8	C <sub>3</sub> H <sub>4</sub> O	70.0898	2,5-dithiofuran	9.21	22704-38-7	C <sub>3</sub> H <sub>10</sub>	94.1543	3-( <i>cis</i> -ethylidene)-1-cyclopentene	7.94	7.94
109-98-8	C <sub>3</sub> H <sub>6</sub> N <sub>2</sub>	70.0931	1-pyrazoline	8.10	121839-51-8	C <sub>3</sub> H <sub>10</sub>	94.1543	(1 $\alpha$ ,4 $\alpha$ ,5 $\beta$ )-5-methyl-2-methylenebicyclo[2.1.0]pentane	7.08	7.08
2721-43-9	C <sub>3</sub> H <sub>6</sub> N <sub>2</sub>	70.0931	1-pyrazoline	8.92	591-54-8	C <sub>3</sub> H <sub>5</sub> N <sub>3</sub>	95.1026	4-aminopyrimidine	8.96	8.96
4923-79-9	C <sub>3</sub> H <sub>9</sub> N	71.1210	<i>N</i> -methylazetidine	7.81	1192-21-8	C <sub>3</sub> H <sub>7</sub> N <sub>3</sub>	97.1185	1-methyl-5-aminopyrazole	7.72	7.72
4901-76-2	C <sub>3</sub> H <sub>8</sub> N <sub>2</sub>	72.1090	3,3-dimethyldiaziridine	8.85	1904-31-0	C <sub>3</sub> H <sub>7</sub> N <sub>3</sub>	97.1185	1-methyl-3-aminopyrazole	7.56	7.56
16955-35-4	C <sub>3</sub> H <sub>5</sub> N	79.0999	bicyclo[1.1.0]butane-1-carbonitrile	9.44	6794-96-3	C <sub>3</sub> H <sub>10</sub> N <sub>2</sub>	98.1463	2-methyl-1,5-diazabicyclo[3.1.0]hexane	7.89	7.89
3696-36-4	C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	80.0880	1,1-dicyanoethane	12.32	53971-47-4	C <sub>3</sub> H <sub>10</sub> S	102.198	trimethylthiirane	8.48	8.48
287-12-7	C <sub>3</sub> H <sub>8</sub>	80.1277	tricyclo[3.1.0.0 <sup>2,6</sup> ]hexane	8.70	13188-85-7	C <sub>3</sub> H <sub>10</sub> S	102.198	3,3-dimethylthietane	8.47	8.47
59660-65-0	C <sub>3</sub> H <sub>8</sub>	80.1277	<i>trans</i> -2,3,4-hexatriene	8.32	539-79-7	C <sub>3</sub> H <sub>8</sub>	104.1491	heptafulvene	7.49	7.49
50786-62-4	C <sub>3</sub> H <sub>8</sub>	80.1277	ethynylcyclobutane	9.53	502-86-3	C <sub>8</sub> H <sub>8</sub>	104.1491	3,6-bis(methylene)-1,4-cyclohexadiene	7.84	7.84
822-41-3	C <sub>8</sub> H <sub>8</sub>	80.1277	bicyclo[2.1.1]hex-2-ene	8.58	38898-42-9	C <sub>8</sub> H <sub>8</sub>	104.1491	3-methylenetetraacyclo[3.2.0.0.2 <sup>7,0</sup> ]heptane	7.75	7.75



Table 3. Continued

CAS-RN	formula	MW g·mol <sup>-1</sup>	compound	G4 AIE eV	formula	MW g·mol <sup>-1</sup>	compound	G4 AIE eV
14296-80-1	C <sub>6</sub> H <sub>8</sub>	80.1277	1,2-bis(methylene)cyclobutane	8.67	C <sub>8</sub> H <sub>8</sub>	104.1491	2a,2b,4a,4b-tetrahydrocyclopropa[cd]pentalene	8.24
693-98-1	C <sub>4</sub> H <sub>6</sub> N <sub>2</sub>	82.1038	2-methyl-1H-imidazole	8.37	C <sub>8</sub> H <sub>10</sub>	106.1650	bicyclo[3.3.0]octa-2,6-diene	9.01
16327-38-1	C <sub>6</sub> H <sub>10</sub>	82.1436	3,3-dimethylcyclobutene	9.24	C <sub>8</sub> H <sub>10</sub>	106.1650	7-methylenecyclo[3.2.0]hept-1-ene	8.27
930-25-6	C <sub>6</sub> H <sub>10</sub>	82.1436	1,3-dimethylcyclo[1.1.0]butane	7.94	C <sub>8</sub> H <sub>10</sub>	106.1650	5-methylenecyclo[2.2.1]hept-2-ene	8.58
4372-94-5	C <sub>6</sub> H <sub>10</sub>	82.1436	1,1-dimethyl-2-methylenecyclopropane	8.83	C <sub>8</sub> H <sub>10</sub>	106.1650	2,3-bis(methylene)bicyclo[2.2.0]hexane	8.52
15506-53-3	C <sub>4</sub> H <sub>4</sub> O <sub>2</sub>	84.0734	cyclobutane-1,3-dione	9.71	C <sub>8</sub> H <sub>10</sub>	106.1650	1-methyltricyclo[4.1.0.0 <sup>2,7</sup> ]hept-3-ene	8.08
n/a	C <sub>4</sub> H <sub>4</sub> O <sub>2</sub>	84.0734	3(2H)-furanone	9.54	C <sub>8</sub> H <sub>10</sub>	106.1650	1-methylnorbornadiene	8.29
20825-71-2	C <sub>4</sub> H <sub>4</sub> O <sub>2</sub>	84.0734	2(3H)-furanone	9.28	C <sub>8</sub> H <sub>10</sub>	108.1809	antitricyclo[4.2.0.0 <sup>2,5</sup> ]octane	8.40
4388-03-8	C <sub>4</sub> H <sub>6</sub> N <sub>2</sub>	84.1197	1,1'-biaziridine	8.03	C <sub>7</sub> H <sub>10</sub> O	110.1537	norbornan-7-one	8.79
872-36-6	C <sub>3</sub> H <sub>2</sub> O <sub>3</sub>	86.0462	1,3-dioxol-2-one	9.64	C <sub>3</sub> H <sub>7</sub> N <sub>5</sub>	113.1212	5-(dimethylamino)tetrazole	8.55
4362-24-7	C <sub>4</sub> H <sub>6</sub> O <sub>2</sub>	86.0892	4-methylene-1,3-dioxolane	8.69	C <sub>8</sub> H <sub>10</sub> S	114.209	7-thiabicyclo[4.1.0]heptane	8.52
5076-19-7	C <sub>5</sub> H <sub>10</sub> O	86.1323	α-trimethylethylene oxide	9.27	C <sub>6</sub> H <sub>17</sub> S	116.224	2-(1,1-dimethylethyl)thiirane	8.60
1120-59-8	C <sub>4</sub> H <sub>6</sub> S	86.155	2,3-dithiothiophene	8.00	C <sub>4</sub> H <sub>6</sub> S <sub>2</sub>	118.220	dihydro-2(3H)-thiophenethione	8.30
22438-40-0	C <sub>4</sub> H <sub>8</sub> S	88.171	3-methylthietane	8.53	C <sub>4</sub> H <sub>8</sub> S <sub>2</sub>	120.236	4-methyl-1,3-dithiolane	8.56
3772-13-2	C <sub>4</sub> H <sub>8</sub> S	88.171	2,2-dimethylthiirane	8.66	C <sub>4</sub> H <sub>8</sub> S <sub>2</sub>	120.236	4-methyl-1,2-dithiolane	7.68
17837-41-1	C <sub>4</sub> H <sub>8</sub> S	88.171	2-methylthietane	8.51	C <sub>4</sub> H <sub>8</sub> S <sub>2</sub>	120.236	3-methyl-1,2-dithiolane	7.66
4646-69-9	C <sub>7</sub> H <sub>6</sub>	90.1225	bicyclo[4.1.0]hepta-1,3,5-triene	8.81	C <sub>4</sub> H <sub>8</sub> S <sub>2</sub>	120.236	2-methyl-1,3-dithiacyclopentane	8.57
35295-58-0	C <sub>7</sub> H <sub>6</sub>	90.1225	bicyclo[3.2.0]hepta-1,4,6-triene	8.57	C <sub>4</sub> H <sub>4</sub> S <sub>2</sub>	140.226	thieno[3,4-b]thiophene	7.88
35618-58-7	C <sub>7</sub> H <sub>8</sub>	92.1384	tricyclo[4.1.0.0 <sup>2,7</sup> ]hept-3-ene	8.35	C <sub>4</sub> H <sub>4</sub> S <sub>2</sub>	140.226	dithio-p-benzoquinone	8.75
50861-26-2	C <sub>7</sub> H <sub>8</sub>	92.1384	tetracyclo[4.1.0.0 <sup>2,4</sup> .0 <sup>3,5</sup> ]heptane	8.41	C <sub>4</sub> H <sub>4</sub> S <sub>3</sub>	148.270	4-methyl-3H-1,2-dithiole-3-thione	8.18
79356-83-5	C <sub>7</sub> H <sub>8</sub>	92.1384	antitricyclo[3.2.0.0 <sup>2,4</sup> ]hept-6-ene	8.63				

limit of this range and in excellent agreement with the value of 8.3 eV by Bowers.<sup>50</sup>

A substantial number of well-known compounds still lack fundamental physical property determinations. AIEs were estimated at the G4 level for 85 organic compounds for which no experimental values were present in the NIST database (Table 3). These compounds are generally conformationally constrained molecules with a number of ringed/bridged derivatives being of broad interest in organic chemistry on the grounds of charged aromaticity/homoaromaticity. On the basis of our benchmarking efforts provided in Tables 1 and 2, neither the G4 nor WBD method exhibit any systematic bias in AIE estimation, and both methods have error metrics at or below chemical accuracy limits when compared against high quality experimental data. Consequently, we expect the AIEs presented in Table 3 to achieve effective chemical accuracy.

## Conclusions

The Gaussian-4 (G4) composite method was used to estimate gas phase (298.15 K, 101.325 kPa) AIEs for 236 organic compounds. The WBD level of theory was also employed to estimate AIEs for a subset of 17 compounds. Excellent agreement between the G4 and the WBD AIE estimates was obtained. For compounds having well-constrained experimental AIEs, both levels of theory achieve effective chemical accuracy.

## Supporting Information Available:

Optimized geometries, energies at each stage of the optimization process, and frequency coordinates for the cationic forms and molecular enthalpies and free energies for the neutral and cationic forms, as well as available experimental AIEs for all compounds investigated. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## Literature Cited

- (1) McNaught, A. D.; Wilkinson, A. *IUPAC Compendium of Chemical Terminology*, 2nd ed.; Blackwell Scientific Publications: Oxford, 1997.
- (2) Mulliken, R. S. A New Electroaffinity Scale: Together with Data on Valence States and on Valence Ionization Potentials and Electron Affinities. *J. Chem. Phys.* **1934**, *2*, 782–793.
- (3) Mulliken, R. S. Electronic Structures of Molecules XI. Electroaffinity, Molecular Orbitals and Dipole Moments. *J. Chem. Phys.* **1935**, *3*, 573–585.
- (4) Parr, R. G.; Pearson, R. G. Absolute Hardness: Companion Parameter to Absolute Electronegativity. *J. Am. Chem. Soc.* **1983**, *105*, 7512–7516.
- (5) Pearson, R. G. Absolute Electronegativity and Absolute Hardness of Lewis Acids and Bases. *J. Am. Chem. Soc.* **1985**, *107*, 6801–6806.
- (6) Parr, R. G.; Chattaraj, P. K. Principle of Maximum Hardness. *J. Am. Chem. Soc.* **1991**, *113*, 1854–1855.
- (7) Parr, R. G.; Szentpaly, L. V.; Liu, S. Electrophilicity Index. *J. Am. Chem. Soc.* **1999**, *121*, 1922–1924.
- (8) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; John Wiley and Sons: New York, 2003.
- (9) Fahlman, B. D. *Materials Chemistry*; Springer: New York, 2008.
- (10) DeHoff, R. T. *Thermodynamics in Materials Science*; Taylor & Francis: Boca Raton, 2006.
- (11) Eriksson, L. A. *Theoretical Biochemistry: Processes and Properties of Biological Systems*; Elsevier: New York, 2001.
- (12) Riley, K. E.; Op't Holt, B. T.; Merz, K. M. Critical Assessment of the Performance of Density Functional Methods for Several Atomic and Molecular Properties. *J. Chem. Theory Comput.* **2007**, *3*, 407–433.
- (13) De Prof, F.; Geerlings, P. Calculation of Ionization Energies, Electron Affinities, Electronegativities, and Hardnesses Using Density Functional Methods. *J. Chem. Phys.* **1997**, *106*, 3270–3279.
- (14) Zhao, Y.; Truhlar, D. G. Exploring the Limit of Accuracy of the Global Hybrid Meta Density Functional for Main-Group Thermochemistry, Kinetics, and Noncovalent Interactions. *J. Chem. Theory Comput.* **2008**, *4*, 1849–1868.
- (15) Jursic, B. S. A Density Functional Theory Evaluation of the Ionization Energies of Alkanes, Cycloalkanes and Their Unsaturated Analogs. *J. Mol. Struct.* **1998**, *452*, 145–152.

- (16) Rohrdanz, M. A.; Herbert, J. M. Simultaneous Benchmarking of Ground- and Excited-State Properties with Long-Range-Corrected Density Functional Theory. *J. Chem. Phys.* **2008**, *129*, 034107.
- (17) Zhan, C. G.; Nichols, J. A.; Dixon, D. A. Ionization Potential, Electron Affinity, Electronegativity, Hardness, and Electron Excitation Energy: Molecular Properties from Density Functional Theory Orbital Energies. *J. Phys. Chem. A* **2003**, *107*, 4184–4195.
- (18) Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. Gaussian-1 Theory: A General Procedure for Prediction of Molecular Energies. *J. Chem. Phys.* **1989**, *90*, 5622–5629.
- (19) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. Assessment of Gaussian-3 and Density Functional Theories for a Larger Experimental Test Set. *J. Chem. Phys.* **2000**, *112*, 7374–7383.
- (20) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. Assessment of Gaussian-2 and Density Functional Theories for the Computation of Ionization Potentials and Electron Affinities. *J. Chem. Phys.* **1998**, *109*, 42–55.
- (21) Parthiban, S.; Martin, J. M. L. Assessment of W1 and W2 theories for the Computation of Electron Affinities, Ionization Potentials, Heats of Formation, and Proton Affinities. *J. Chem. Phys.* **2001**, *114*, 6014–6029.
- (22) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. Gaussian-4 Theory. *J. Chem. Phys.* **2007**, *126*, 84108–84112.
- (23) Barnes, E. C.; Petersson, G. A.; Montgomery, J. A.; Frisch, M. J.; Martin, J. M. L. Unrestricted Coupled Cluster and Brueckner Doubles Variations of W1 theory. *J. Chem. Theory Comput.* **2009**, *5*, 2687–2693.
- (24) Linstrom, P. J.; Mallard, W. G. *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; National Institute of Standards and Technology: Gaithersburg, MD, 2010; <http://webbook.nist.gov> (retrieved July 30, 2010).
- (25) Halgren, T. A. Merck Molecular Force Field. I. Basis, Form, Scope, Parameterization, and Performance of MMFF94. *J. Comput. Chem.* **1996**, *17*, 490–519.
- (26) Halgren, T. A. Merck Molecular Force Field. III. Molecular Geometries and Vibrational Frequencies for MMFF94. *J. Comput. Chem.* **1996**, *17*, 553–586.
- (27) Halgren, T. A. Merck Molecular Force Field. V. Extension of MMFF94 using Experimental Data, Additional Computational Data, and Empirical Rules. *J. Comput. Chem.* **1996**, *17*, 616–641.
- (28) Halgren, T. A. MMFF VII. Characterization of MMFF94, MMFF94s, and Other Widely Available Force Fields for Conformational Energies and for Intermolecular-Interaction Energies and Geometries. *J. Comput. Chem.* **1999**, *20*, 730–748.
- (29) Halgren, T. A.; Nachbar, R. B. Merck Molecular Force Field. IV. Conformational Energies and Geometries for MMFF94. *J. Comput. Chem.* **1996**, *17*, 587–615.
- (30) Martin, J. M. L.; de Oliveira, G. Towards Standard Methods for Benchmark Quality Ab Initio Thermochemistry - W1 and W2 Theory. *J. Chem. Phys.* **1999**, *111*, 1843–1856.
- (31) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09, Revision A.02*; Gaussian, Inc.: Wallingford, CT, 2009.
- (32) Allouche, A. R. Gabedit: A Graphical User Interface for Computational Chemistry Softwares. *J. Comput. Chem.* **2011**, *32*, 174–182.
- (33) Rayne, S.; Forest, K. Estimated Gas Phase Standard State Enthalpies of Formation for Organic Compounds using the Gaussian-4 (G4) and W1BD Theoretical Methods. *J. Chem. Eng. Data* **2010**, *55*, 5359–5364.
- (34) Luo, Y. R.; Pacey, P. D. Effects of Alkyl Substitution on Ionization Energies of Alkanes and Haloalkanes and on Heats of Formation of Their Molecular Cations. Part 2. Alkanes and Chloro-, Bromo- and Iodoalkanes. *Int. J. Mass Spectrom.* **1992**, *112*, 63–77.
- (35) Flesch, G. D.; Svec, H. J. Fragmentation Reactions in the Mass Spectrometer for C<sub>2</sub>-C<sub>5</sub> Alkanes. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 1187–1199.
- (36) Blais, J. C.; Cottin, M.; Gitton, B. Ionisation Positive et Negative dans le Dimethylsulfoxyde en Phase Gazeuse. *J. Chim. Phys.* **1970**, *67*, 1475.
- (37) Distefano, G.; Foffani, A.; Innorta, G.; Pignataro, S. Electron Impact Ionization Potentials of Some Manganese, Chromium and Tungsten Organometallic Derivatives. *Int. J. Mass Spectrom.* **1971**, *7*, 383–390.
- (38) Potzinger, P.; Stracke, H. U.; Kupper, W.; Gollnick, K. Ionisierungs- und Aufttrittspotentialmessungen an Dialkylsulfoxiden. *Z. Naturforsch., A* **1975**, *30*, 340–347.
- (39) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. *Handbook of HeI Photoelectron Spectra of Fundamental Organic Compounds*; Japan Scientific Society Press: Tokyo, 1981.
- (40) Parkin, J. E.; Innes, K. K. The Vacuum Ultraviolet Spectra of Pyrazine, Pyrimidine, and Pyridazine Vapors. Part I. Spectra Between 1550 Å and 2000 Å. *J. Mol. Spectrosc.* **1965**, *15*, 407–434.
- (41) Yench, A. J.; El-Sayed, M. A. Lowest Ionization Potentials of Some Nitrogen Heterocyclics. *J. Chem. Phys.* **1968**, *48*, 3469–3475.
- (42) Dewar, M. J. S.; Worley, S. D. Photoelectron Spectra of Molecules. II. The Ionization Potentials of Azabenzenes and Azanaphthalenes. *J. Chem. Phys.* **1969**, *51*, 263–267.
- (43) Eland, J. H. D. Photoelectron Spectra of Conjugated Hydrocarbons and Heteromolecules. *Int. J. Mass Spectrom.* **1969**, *2*, 471–484.
- (44) Asbrink, L.; Lindholm, E.; Edqvist, O. Jahn-Teller Effect in the Vibrational Structure of the Photoelectron Spectrum of Benzene. *Chem. Phys. Lett.* **1970**, *5*, 609–612.
- (45) Gleiter, R.; Heilbronner, E.; Hornung, V. Photoelectron Spectra of Azabenzenes and Azanaphthalenes: I. Pyridine, Diazines, s-Triazine and s-Tetrazine. *Helv. Chim. Acta* **1972**, *55*, 255–274.
- (46) Scheps, R.; Florida, D.; Rice, S. A. Comments on the Rydberg Spectrum of Pyrazine. *J. Mol. Spectrosc.* **1972**, *44*, 1–13.
- (47) Piancastelli, M. N.; Keller, P. R.; Taylor, J. W.; Grimm, F. A.; Carlson, T. A. Angular Distribution Parameter as a Function of Photon Energy for Some Mono- and Diazabenzenes and Its Use for Orbital Assignment. *J. Am. Chem. Soc.* **1983**, *105*, 4235–4239.
- (48) Gallegos, E. J.; Kiser, R. W. Electron Impact Spectroscopy of the Four- and Five-Membered, Saturated Heterocyclic Compounds Containing Nitrogen, Oxygen and Sulfur. *J. Phys. Chem.* **1962**, *66*, 136–145.
- (49) Kiser, R. W.; Gallegos, E. J. A Technique for the Rapid Determination of Ionization and Appearance Potentials. *J. Phys. Chem.* **1962**, *66*, 947–948.
- (50) Bowers, M. T. *Gas Phase Ion Chemistry*; Academic Press: New York, 1979.
- (51) Tarasenko, N. A.; Tishenkov, A. A.; Zaikin, V. G.; Volkova, V. V.; Gusel'nikov, L. E. Adiabatic Ionization Energy of Methylenimine. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1986**, *10*, 2196–2202.
- (52) Lias, S. G. Ionization Energy Evaluation. 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, 2010; <http://webbook.nist.gov> (retrieved July 30, 2010).
- (53) Lias, S. G.; Levin, R. D.; Kafafi, S. A. Ionization Energy Evaluation. 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, 2010; <http://webbook.nist.gov> (retrieved July 30, 2010).
- (54) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. Ionization Energy Evaluation. 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, 2010; <http://webbook.nist.gov> (retrieved July 30, 2010).

Received for review September 7, 2010. Accepted December 9, 2010. This work was made possible by the facilities of the Western Canada Research Grid (project 100185), the Shared Hierarchical Academic Research Computing Network (project aqn-965), and Compute/Calcul Canada.

JE100913F