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

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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.[1] 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,[2−7] but they are also widely employed toward redox processes in natural, engineered, and biological systems and in the design of new materials.[8−11]

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.[18−21] 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.[22] 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.[23]

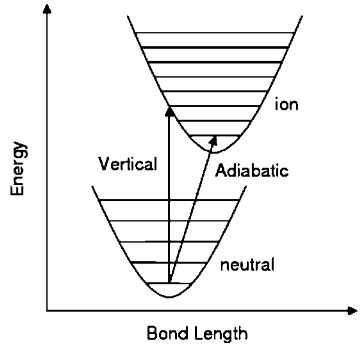

Figure 1. Schematic potential energy diagram for a diatomic molecule illustrating the difference between adiabatic and vertical ionization energies. Adapted from http://cccbdb.nist.gov/adiabatic.asp.

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.[24] 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 MMFF94[25−29] 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

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

		MW		AIE/eV		
CAS-RN	formula	$g \cdot mol^{-1}$	name	expt.	G4	W1BD
74-86-2	C_2H_2	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_2O	30.0260	formaldehyde	10.88 ± 0.01	10.89	10.91
74-89-5	CH_5N	31.0571	methylamine	8.9 ± 0.1	9.05	9.06
115-07-1	C_3H_6	42.0797	propene	9.73 ± 0.01	9.77	9.76
124-38-9	CO_2	44.0095	carbon dioxide	13.777 ± 0.001	13.78	13.84
75-21-8	C_2H_4O	44.0526	ethylene oxide	10.56 ± 0.01	10.58	10.60
75-07-0	C_2H_4O	44.0526	acetaldehyde	10.2290 ± 0.0007	10.23	10.26
64-18-6	CH_2O_2	46.0254	formic acid	11.33 ± 0.01	11.30	11.35
75-02-5	C_2H_3F	46.0436	fluoroethene	10.36 ± 0.01	10.35	10.37
74-93-1	CH_4S	48.107	methanethiol	9.439 ± 0.005	9.45	9.45
74-87-3	CH_3Cl	50.488	chloromethane	11.26 ± 0.03	11.26	11.30
75-10-5	CH_2F_2	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_2H_3Cl	62.498	chloroethene	9.99 ± 0.02	9.98	10.02
353-50-4	CF_2O	66.0069	carbonic difluoride	13.04 ± 0.03	12.96	13.04

[a] Experimental values are the evaluated AIEs taken from the compendium of Lias[52] in the NIST Database.

inputs for Gaussian-4 (G4)[22] and W1BD[23,30] composite method calculations with Gaussian 09.[31]

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.[32] 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.[33] 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 acylic, 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[34] and 10.50 ± 0.05) eV.[35] 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,[36] 9.20 ± 0.05 eV,[37] 9.08 ± 0.09 eV,[38] and 9.10 eV.[39] 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,[40] 9.29 ± 0.01 eV,[41] 9.36 eV,[42] 9.28 ± 0.05 eV,[43] 9.216 eV,[44] 9.29 eV,[45] 9.28 ± 0.01 eV,[46] and 9.0 eV.[47] 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,[48] 8.9 eV,[49] 8.3 eV,[50] and 8.63 ± 0.02 eV[51] 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[a]

		MW		AIE/eV				MW		AIE/eV	
CAS-RN	formula	g·mol^{-1}	name	expt	G4	CAS-RN	formula	g·mol^{-1}	name	expt	G4
689-97-4	C_4H_4	52.0746	1-buten-3-yne	9.58 ± 0.02	9.61	110-54-3	C_6H_{14}	86.1754	hexane	10.13 ± 0.10	10.00
2873-50-9	C_4H_4	52.0746	1,2,3-butatriene	9.15 to 9.40	9.16	72323-66-1	C_7H_6	90.1225	1,1-diethynylcyclopropane	8.9	8.95
1120-53-2	C_4H_4	52.0746	cyclobutadiene	8.16 to 9.55	8.06	27041−32−3	C_7H_6	90.1225	5-ethenylidene-1,3-cyclopentadiene	8.88	8.23
107-13-1	C_3H_3N	53.0626	2-propenenitrile	10.91 ± 0.01	10.96	59502-33-9	C_7H_6	90.1225	*cis*-1,2-diethynylcyclopropane	8.90	8.92
157-33-5	C_4H_6	54.0904	bicyclo[1.1.0]butane	8.70 ± 0.01	8.79	35295-57-9	C_7H_6	90.1225	*trans*-1,2-diethynylcyclopropane	9.00	8.89
822-35-5	C_4H_6	54.0904	cyclobutene	9.43 ± 0.02	9.47	4513-94-4	$C_5H_4N_2$	92.0987	pyrrole-2-carbonitrile	8.7	8.86
6788-85-8	C_3H_5N	55.0785	1-azetine	9.30	9.31	121-46-0	C_7H_8	92.1384	2,5-norbornadiene	8.38 ± 0.04	8.39
115-11-7	C_4H_8	56.1063	2-methyl-1-propene	9.22 ± 0.02	9.24	3217-87-6	C_7H_8	92.1384	3-methylene-1,4-cyclohexadiene	8.6	8.12
590-18-1	C_4H_8	56.1063	*cis*-2-butene	9.11 ± 0.01	9.14	67254-49-3	C_7H_8	92.1384	5-methylenebicyclo[2.2.0]hex-2-ene	8.8	8.80
624-64-6	C_4H_8	56.1063	*trans*-2-butene	9.10 ± 0.01	9.15	2422-86-8	C_7H_8	92.1384	bicyclo[3.2.0]hepta-2,6-diene	8.35	8.68
1072-44-2	C_3H_7N	57.0944	1-methylaziridine	8.7	8.67	278-06-8	C_7H_8	92.1384	quadricyclane	7.80 to 8.70	7.66
503-29-7	C_3H_7N	57.0944	azetidine	8.3 to 9.1	8.32	765-46-8	C_7H_8	92.1384	spiro[2,4]hepta-4,6-diene	8.14	8.11
75-56-9	C_3H_6O	58.0791	methyloxirane	10.22 ± 0.02	10.09	22635-78-5	C_7H_8	92.1384	spiro[3.3]hepta-2,5-diene	9.02	9.01
503-30-0	C_3H_6O	58.0791	oxetane	9.65 ± 0.01	9.69	108-88-3	C_7H_8	92.1384	toluene	8.828 ± 0.001	8.86
75-56-9	C_3H_6O	58.0791	propylene oxide	10.22 ± 0.02	10.24	109-06-8	C_6H_7N	93.1265	2-methylpyridine	9.02 to 9.40	9.01
64-19-7	$C_2H_4O_2$	60.0520	acetic acid	10.65 ± 0.02	10.62	62-53-3	C_6H_7N	93.1265	aniline	7.720 ± 0.002	7.74
75-38-7	$C_2H_2F_2$	64.0341	1,1-difluoroethene	10.29 ± 0.0	10.27	108-95-2	C_6H_6O	94.1112	phenol	8.49 ± 0.02	8.53
21986-03-8	C_5H_4	64.0853	1,2,3,4-pentatetraene	8.67	8.77	51549-86-1	C_7H_{10}	94.1543	1-methyl-1,2-propadienylcyclopropane	8.83	8.28
24442-69-1	C_5H_4	64.0853	penta-1,4-diyne	10.10 to 10.27	10.31	498-66-8	C_7H_{10}	94.1543	2-norbornene	8.60 to 9.05	8.80
1574-40-9	C_5H_6	66.1011	(*Z*)-3-penten-1-yne	9.11	9.11	4125-18-2	C_7H_{10}	94.1543	5,5-dimethyl-1,3-cyclopentadiene	8.20 to 8.22	8.35
646-05-9	C_5H_6	66.1011	1-penten-3-yne	9.00 ± 0.01	9.00	51273-50-8	C_7H_{10}	94.1543	tricyclo[3.1.1.0^{3,6}]heptane	8.7	8.71
542-92-7	C_5H_6	66.1011	1,3-cyclopentadiene	8.57 ± 0.01	8.59	174-73-2	C_7H_{10}	94.1543	tricyclo[4.1.0.0^{1,3}]heptane	8.6	8.54
78-80-8	C_5H_6	66.1011	2-methyl-1-buten-3-yne	9.25 ± 0.02	9.25	24108-33-6	$C_4H_5N_3$	95.1026	3-methyl-1,2,4-triazine	8.6	8.77
5164-35-2	C_5H_6	66.1011	bicyclo[2.1.0]pent-2-ene	8.0	8.15	2721-32-6	$C_5H_8N_2$	96.1304	2,3-diazabicyclo[2.2.1]-hept-2-ene	8.45	8.54
6746-94-7	C_5H_6	66.1011	cyclopropylacetylene	8.7	9.19	75-35-4	$C_2H_2Cl_2$	96.943	1,1-dichloroethene	9.81 ± 0.04	9.78
109-97-7	C_4H_5N	67.0892	pyrrole	8.207 ± 0.005	8.22	156-59-2	$C_2H_2Cl_2$	96.943	*cis*-1,2-dichloroethene	9.66 ± 0.01	9.61
504-64-3	C_3O_2	68.0309	carbon suboxide	10.60	10.66	156-60-5	$C_2H_2Cl_2$	96.943	*trans*-1,2-dichloroethene	9.64 ± 0.02	9.57
110-00-9	C_4H_4O	68.0740	furan	8.88 ± 0.01	8.89	75-44-5	CCl_2O	98.916	phosgene	11.2 to 11.7	11.50
288-32-4	$C_3H_4N_2$	68.0773	1*H*-imidazole	8.81 ± 0.01	8.82	116-14-3	C_2F_4	100.0150	tetrafluoroethene	10.14 ± 0.07	10.05
288-13-1	$C_3H_4N_2$	68.0773	1*H*-pyrazole	9.25 to 9.38	9.28	1072-20-4	C_8H_6	102.1332	2,4,6-octatriyne	8.60	8.53
185-94-4	C_5H_8	68.1170	bicyclo[2.1.0]pentane	8.7	8.66	4026-23-7	C_8H_6	102.1332	bicyclo[4.2.0]octa-1,3,5,7-tetraene	7.5	7.76
157-40-4	C_5H_8	68.1170	spiropentane	9.26	9.39	536-74-3	C_8H_6	102.1332	phenylacetylene	8.81 to 8.90	8.84
109-96-6	C_4H_7N	69.1051	2,5-dihydro-1*H*-pyrrole	8.0	8.08	20380-31-8	C_8H_8	104.1491	(1α,2β,5β,6α)-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene	8.27	8.68
75-46-7	CHF_3	70.0138	trifluoromethane	13.86	13.77	33284-11-6	C_8H_8	104.1491	1,5-dihydropentalene	7.86	7.86
1467-79-4	$C_3H_6N_2$	70.0931	dimethylcyanamide	9.0	9.20	37846-63-2	C_8H_8	104.1491	7-methylenebicyclo[2.2.1]hepta-2,5-diene	8.5	8.41
109-99-9	C_4H_8O	72.1057	tetrahydrofuran	9.40 ± 0.02	9.42	500-24-3	C_8H_8	104.1491	bicyclo[2.2.2]octa-2,5,7-triene	7.95 to 8.24	8.23
78-78-4	C_5H_{12}	72.1488	isopentane	10.32 ± 0.05	10.02	694-87-1	C_8H_8	104.1491	bicyclo[4.2.0]octa-1,3,5-triene	8.74	8.67
463-82-1	C_5H_{12}	72.1488	neopentane	≤10.30 ± 0.08	10.18	80339-91-9	C_8H_8	104.1491	cycloocta-1,3-dien-6-yne	8.5	8.60
109-66-0	C_5H_{12}	72.1488	pentane	10.28 ± 0.10	10.21	68344-46-7	C_8H_8	104.1491	cycloocta-1,5-dien-3-yne	8.2	8.37
1071-98-3	C_4N_2	76.0562	2-butynedinitrile	11.40 to 11.81	11.94	20656-23-9	C_8H_8	104.1491	pentacyclo[3.3.0.0.^{2,4}0.^{3,7}0^{6,8}]octane	8.18	8.25
16668-68-1	C_6H_4	76.0960	(*E*)-hexa-1,5-diyne-3-ene	9.07	9.08	100-42-5	C_8H_8	104.1491	styrene	8.464 ± 0.001	8.49
16668-67-0	C_6H_4	76.0960	(*Z*)-hexa-1,5-diyne-3-ene	9.10	9.11	3227-91-6	C_8H_8	104.1491	tetrakis(methylene)cyclobutane	8.35	8.35
6929-94-8	C_6H_4	76.0960	hex-3-en-1,5-diyne	9.6	9.08	35438-35-8	C_8H_8	104.1491	tricyclo[4.1.1.0^{7,8}]octa-2,4-diene	7.9	8.07
75-15-0	CS_2	76.141	carbon disulfide	10.073 ± 0.005	10.11	75-72-9	$CClF_3$	104.459	chlorotrifluoromethane	12.6 ± 0.4	12.42
5291-90-7	C_6H_6	78.1118	3,4-dimethylenecyclobut-1-ene	8.80	8.80	63001-13-8	C_8H_{10}	106.1650	1,5-dimethyl-3-exomethylenetricyclo[2.1.0.0]pentane	8.0	7.65
71-43-2	C_6H_6	78.1118	benzene	9.24378 ± 0.00007	9.29	4096-95-1	C_8H_{10}	106.1650	bicyclo[3.2.1]octa-2,6-diene	8.44	8.32
5649-95-6	C_6H_6	78.1118	bicyclo[2.2.0]hexa-2,5-diene	9.0	8.93	102575-26-8	C_8H_{10}	106.1650	tricyclo[4.1.1.0^{7,8}]oct-2-ene	8.2	8.24
3227-90-5	C_6H_6	78.1118	tris(methylene)cyclopropane	9.0	9.08	102575-25-7	C_8H_{10}	106.1650	tricyclo[4.1.1.0^{7,8}]oct-3-ene	8.3	8.41
67-68-5	C_2H_6OS	78.133	dimethyl sulfoxide	9.08 to 9.90	8.86	108-90-7	C_6H_5Cl	112.557	chlorobenzene	9.07 ± 0.02	9.09
290-37-9	$C_4H_4N_2$	80.0880	pyrazine	9.00 to 9.36	9.28	372-18-9	$C_6H_4F_2$	114.0928	*m*-difluorobenzene	9.33 ± 0.02	9.34
289-80-5	$C_4H_4N_2$	80.0880	pyridazine	8.74 ± 0.11	8.70	367-11-3	$C_6H_4F_2$	114.0928	*o*-difluorobenzene	9.29 ± 0.01	9.30
289-95-2	$C_4H_4N_2$	80.0880	pyrimidine	9.33 ± 0.07	9.39	540-36-3	$C_6H_4F_2$	114.0928	*p*-difluorobenzene	9.1589 ± 0.0005	9.15

Table 2. Continued

		MW		AIE/eV				MW		AIE/eV	
CAS-RN	formula	g·mol^{-1}	name	expt	G4	CAS-RN	formula	g·mol^{-1}	name	expt	G4
96-39-9	C_6H_8	80.1277	1-methyl-1,3-cyclopentadiene	8.40 ± 0.02	8.16	673-32-5	C_9H_8	116.1598	1-propynylbenzene	8.42	8.43
2045-78-5	C_6H_8	80.1277	1,3-bis(methylene)cyclobutane	8.7	9.11	79-38-9	C_2ClF_3	116.470	chlorotrifluoroethene	9.81 ± 0.03	9.76
930-26-7	C_6H_8	80.1277	3-methylenecyclopentene	8.40	8.32	67-66-3	$CHCl_3$	119.378	trichloromethane	11.37 ± 0.02	11.42
96-38-8	C_6H_8	80.1277	5-methyl-1,3-cyclopentadiene	8.45	8.47	75-71-8	CCl_2F_2	120.914	difluorodichloromethane	12.0 ± 0.2	11.73
3097-63-0	C_6H_8	80.1277	bicyclo[2.2.0]hex-2-ene	9.0	8.90	79-01-6	C_2HCl_3	131.388	trichloroethene	9.46 ± 0.02	9.41
290-38-0	$C_3H_3N_3$	81.0760	1,2,4-triazine	9.2	9.08	83589-40-6	CCl_3F	137.368	fluorotrichloromethane	11.68 ± 0.13	11.69
78104-88-8	C_5H_7N	81.1158	1-methylcyclopropanecarbonitrile	10.53	9.92	81044-78-2	$C_6H_4S_2$	140.226	benzodithiete	8.15	8.32
359-11-5	C_2HF_3	82.0245	trifluoroethene	10.14	10.10	251-41-2	$C_6H_4S_2$	140.226	thieno[3,2-b]thiophene	8.10	8.11
420-46-2	$C_2H_3F_3$	84.0404	1,1,1-trifluoroethane	13.3	12.48	541-73-1	$C_6H_4Cl_2$	147.002	*m*-dichlorobenzene	9.10 ± 0.02	9.13
290-67-5	$C_4H_4O_2$	84.0734	1,4-dioxin	7.75	7.85	95-50-1	$C_6H_4Cl_2$	147.002	*o*-dichlorobenzene	9.06 ± 0.02	9.05
674-82-8	$C_4H_4O_2$	84.0734	4-methylene-2-oxetanone	9.6	9.34	106-46-7	$C_6H_4Cl_2$	147.002	*p*-dichlorobenzene	8.92 ± 0.03	8.91
674-82-8	$C_4H_4O_2$	84.0734	diketene	9.6	9.34	75-87-6	$C_2HC_{l3}O$	147.388	trichloroacetaldehyde	10.9	10.36
110-02-1	C_4H_4S	84.140	thiophene	8.86 ± 0.02	8.89	56-23-5	CCl_4	153.823	tetrachloromethane	11.47 ± 0.01	11.53
75-09-2	CH_2Cl_2	84.933	dichloromethane	11.33 ± 0.04	11.10	127-18-4	C_2Cl_4	165.833	tetrachloroethene	9.326 ± 0.001	9.24
1708-32-3	C_4H_6S	86.155	2,5-dihydrothiophene	8.4	8.49	120-82-1	$C_6H_3Cl_3$	181.447	1,2,4-trichlorobenzene	9.04 ± 0.03	8.97

[a] Single experimental values are either the evaluated AIEs taken from the compendia of Lias[52] and Lias et al.[53] 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

		MW		G4 AIE			MW		G4 AIE
CAS-RN	formula	g·mol^{-1}	compound	eV	CAS-RN	formula	g·mol^{-1}	compound	eV
4095-06-1	C_4H_4	52.0746	methylenecyclopropene	8.13	3839-50-7	C_7H_8	92.1384	6-methylfulvene	8.10
58208-49-4	C_4H_4	52.0746	bicyclo[1.1.0]but-1(3)-ene	9.16	31357-71-8	C_6H_7N	93.1265	bicyclo[2.1.0]pentane-1-carbonitrile	9.26
3100-04-7	C_4H_6	54.0904	1-methylcyclopropene	9.11	287-13-8	C_7H_{10}	94.1543	tricyclo[4.1.0.0^{2,7}]heptane	8.35
54376-32-8	C_3H_5N	55.0785	cyclopropanimine	8.80	187-26-8	C_7H_{10}	94.1543	tricyclo[4.1.0.0^{2,4}]heptane	8.80
59078-44-3	C_4H_4O	68.0740	cyclopropylidenemethanone	8.75	87304-84-5	C_7H_{10}	94.1543	*syn*-tricyclo[3.2.0.0^{2,4}]heptane	8.04
33898-53-2	$C_3H_4N_2$	68.0773	2-aziridinecarbonitrile	10.22	121733-05-9	C_7H_{10}	94.1543	*endo*-2-methylene-5-methylbicyclo[2.1.0]pentane	8.04
18631-84-0	C_5H_8	68.1170	methylmethylenecyclopropane	9.22	54140-30-6	C_7H_{10}	94.1543	cyclopentyl acetylene	9.66
18631-83-9	C_5H_8	68.1170	ethylidenecyclopropane	9.02	10563-10-7	C_7H_{10}	94.1543	bicyclo[3.2.0]hept-1(5)-ene	8.40
14309-32-1	C_5H_8	68.1170	1,2-dimethylcyclopropene	8.60	22630-75-7	C_7H_{10}	94.1543	bicyclo[3.2.0]hept-1-ene	8.33
1489-60-7	C_5H_8	68.1170	1-methylcyclobutene	8.92	28102-61-6	C_7H_{10}	94.1543	antitricyclo[3.2.0.0^{2,4}]heptane	8.48
n/a	C_4H_6O	70.0898	3-methyleneoxetane	9.49	74503-34-7	C_7H_{10}	94.1543	5,5-dimethylbicyclo[2.1.0]pent-2-ene	7.87
1708-29-8	C_4H_6O	70.0898	2,5-dihydrofuran	9.21	22704-38-7	C_7H_{10}	94.1543	3-(*cis*-ethylidene)-1-cyclopentene	7.94
109-98-8	$C_3H_6N_2$	70.0931	2-pyrazoline	8.10	121839-51-8	C_7H_{10}	94.1543	(1α,4α,5*β*)-5-methyl-2-methylenebicyclo[2.1.0]pentane	7.08
2721-43-9	$C_3H_6N_2$	70.0931	1-pyrazoline	8.92	591-54-8	$C_4H_5N_3$	95.1026	4-aminopyrimidine	8.96
4923-79-9	C_4H_9N	71.1210	*N*-methylazetidine	7.81	1192-21-8	$C_4H_7N_3$	97.1185	1-methyl-5-aminopyrazole	7.72
4901-76-2	$C_3H_8N_2$	72.1090	3,3-dimethyldiaziridine	8.85	1904-31-0	$C_4H_7N_3$	97.1185	1-methyl-3-aminopyrazole	7.56
16955-35-4	C_5H_5N	79.0999	bicyclo[1.1.0]butane-1-carbonitrile	9.44	6794-96-3	$C_5H_{10}N_2$	98.1463	2-methyl-1,5-diazabicyclo[3.1.0]hexane	7.89
3696-36-4	$C_4H_4N_2$	80.0880	1,1-dicyanoethane	12.32	53971-47-4	$C_5H_{10}S$	102.198	trimethylthiirane	8.48
287-12-7	C_6H_8	80.1277	tricyclo[3.1.0.0^{2,6}]hexane	8.70	13188-85-7	$C_5H_{10}S$	102.198	3,3-dimethylthietane	8.47
59660-65-0	C_6H_8	80.1277	*trans*-2,3,4-hexatriene	8.32	539-79-7	C_8H_8	104.1491	heptafulvene	7.49
50786-62-4	C_6H_8	80.1277	ethynylcyclobutane	9.53	502-86-3	C_8H_8	104.1491	3,6-bis(methylene)-1,4-cyclohexadiene	7.84
822-41-3	C_6H_8	80.1277	bicyclo[2.1.1]hex-2-ene	8.58	38898-42-9	C_8H_8	104.1491	3-methylenetetracyclo[3.2.0.0.^{2,7}0^{4,6}]heptane	7.75

Table 3. Continued

		MW		G4 AIE			MW		G4 AIE
CAS-RN	formula	g·mol^{-1}	compound	eV	CAS-RN	formula	g·mol^{-1}	compound	eV
14296-80-1	C_6H_8	80.1277	1,2-bis(methylene)cyclobutane	8.67	6909-37-1	C_8H_8	104.1491	2*a*,2*b*,4*a*,4*b*-tetrahydrocyclopropa[cd]pentalene	8.24
693-98-1	$C_4H_6N_2$	82.1038	2-methyl-1*H*-imidazole	8.37	41527-66-6	C_8H_{10}	106.1650	bicyclo[3.3.0]octa-2,6-diene	9.01
16327-38-1	C_6H_{10}	82.1436	3,3-dimethylcyclobutene	9.24	75960-13-3	C_8H_{10}	106.1650	7-methylenebicyclo[3.2.0]hept-1-ene	8.27
930-25-6	C_6H_{10}	82.1436	1,3-dimethylbicyclo[1.1.0]butane	7.94	694-91-7	C_8H_{10}	106.1650	5-methylenebicyclo[2.2.1]hept-2-ene	8.58
4372-94-5	C_6H_{10}	82.1436	1,1-dimethyl-2-methylenecyclopropane	8.83	40117-13-3	C_8H_{10}	106.1650	2,3-bis(methylene)bicyclo[2.2.0]hexane	8.52
15506-53-3	$C_4H_4O_2$	84.0734	cyclobutane-1,3-dione	9.71	61772-33-6	C_8H_{10}	106.1650	1-methyltricyclo[4.1.0.0^{2,7}]hept-3-ene	8.08
n/a	$C_4H_4O_2$	84.0734	3(2*H*)-furanone	9.54	n/a	C_8H_{10}	106.1650	1-methylnorbornadiene	8.29
20825-71-2	$C_4H_4O_2$	84.0734	2(3*H*)-furanone	9.28	13027-75-3	C_8H_{12}	108.1809	antitricyclo[4.2.0.0^{2,5}]octane	8.40
4388-03-8	$C_4H_8N_2$	84.1197	1,1′-biaziridine	8.03	10218-02-7	$C_7H_{10}O$	110.1537	norbornan-7-one	8.79
872-36-6	$C_3H_2O_3$	86.0462	1,3-dioxol-2-one	9.64	5422-45-7	$C_3H_7N_5$	113.1212	5-(dimethylamino)tetrazole	8.55
4362-24-7	$C_4H_6O_2$	86.0892	4-methylene-1,3-dioxolane	8.69	286-28-2	$C_6H_{10}S$	114.209	7-thiabicyclo[4.1.0]heptane	8.52
5076-19-7	$C_5H_{10}O$	86.1323	α-trimethylethylene oxide	9.27	37523-44-7	$C_6H_{12}S$	116.224	2-(1,1-dimethylethyl)thiirane	8.60
1120-59-8	C_4H_6S	86.155	2,3-dihydrothiophene	8.00	n/a	$C_4H_6S_2$	118.220	dihydro-2(3*H*)-thiophenthione	8.30
22438-40-0	C_4H_8S	88.171	3-methylthietane	8.53	50363-43-4	$C_4H_8S_2$	120.236	4-methyl-1,3-dithiolane	8.56
3772-13-2	C_4H_8S	88.171	2,2-dimethylthiirane	8.66	n/a	$C_4H_8S_2$	120.236	4-methyl-1,2-dithiolane	7.68
17837-41-1	C_4H_8S	88.171	2-methylthietane	8.51	n/a	$C_4H_8S_2$	120.236	3-methyl-1,2-dithiolane	7.66
4646-69-9	C_7H_6	90.1225	bicyclo[4.1.0]hepta-1,3,5-triene	8.81	5616-51-3	$C_4H_8S_2$	120.236	2-methyl-1,3-dithiacyclopentane	8.57
35295-58-0	C_7H_6	90.1225	bicyclo[3.2.0]hepta-1,4,6-triene	8.57	250-65-7	$C_6H_4S_2$	140.226	thieno[3,4-b]thiophene	7.88
35618-58-7	C_7H_8	92.1384	tricyclo[4.1.0.0^{2,7}]hept-3-ene	8.35	84615-33-8	$C_6H_4S_2$	140.226	dithio-*p*-benzoquinone	8.75
50861-26-2	C_7H_8	92.1384	tetracyclo[4.1.0.0.^{2,4}0^{3,5}]heptane	8.41	3354-41-4	$C_4H_4S_3$	148.270	4-methyl-3*H*-1,2-dithiole-3-thione	8.18
79356-83-5	C_7H_8	92.1384	antitricyclo[3.2.0.0^{2,4}]hept-6-ene	8.63					

limit of this range and in excellent agreement with the value of 8.3 eV by Bowers.[50]

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 W1BD 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 W1BD level of theory was also employed to estimate AIEs for a subset of 17 compounds. Excellent agreement between the G4 and the W1BD 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.

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