Supporting Information

Estimated adiabatic ionization energies for organic compounds using the Gaussian-4 (G4) and W1BD theoretical methods

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Description of G4 Theory

The following description of Gaussian-4 (G4) theory is taken with little adaptation from the following primary reference:

Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. Gaussian-4 Theory. *J. Chem. Phys.* **2007**, *126*, 84108-84112; doi:10.1063/1.2436888

Readers are referred to this source for the original and more complete description.

Gaussian-4 theory is a composite method whereby the following sequence of ab initio molecular orbital calculations are performed to arrive at a total energy for a particular molecular species:

1. The equilibrium structure is obtained at the B3LYP/6-31G(2df,p) level. Spin-restricted theory is used for singlet states and spin-unrestricted theory for others.

2. The B3LYP/6-31G(2df,p) equilibrium structure is used to calculate harmonic frequencies, which are then scaled by a factor of 0.9854.

3. The Hartree-Fock energy limit using a linear two-point extrapolation scheme and Dunning's aug-cc-pVnZ basis sets.

4. A series of single point correlation energy calculations are carried out. The first calculation uses the MP4/6-31G(d) level of theory with corrections for diffuse functions, higher polarization functions,

correlation effects beyond a fourth-order perturbation theory using a coupled cluster theory, and for larger basis set effects and the nonadditivity caused by the assumption of separate basis set extensions for diffuse functions and higher polarization functions.

5. The MP4/6-31G(d) energy and the four correlation corrections are combined in an additive manner along with a correction for the HF limit and a spin-orbit correction.

6. A higher level correction is added to take into account remaining deficiencies in the energy calculations.

7. The total energy at 0 K is obtained by adding the zero-point energy to the total energy.

Description of W1BD Theory

The following description of W1BD theory is taken with little adaptation from the following primary references:

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; doi:10.1063/1.1356014

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; doi:10.1021/ct900260g

Readers are referred to these sources for the original and more complete descriptions.

The W1BD method retains the essential features of W1(RO) theory, but replaces the sequence of ROHF, ROCCSD, and ROCCSD(T) calculations with the BDRef, BD, and BD(T) sequence. The sequence of steps for the W1 method are as follows:

1. A reference geometry is obtained at the B3LYP/cc-pVTZ +1 level.

2. The SCF limit is obtained by geometric extrapolation of the molecular total atomization energy computed using cc-pV*n*Z + 2d*l*f basis sets, where *n*={D,T,Q} and *l*={2,3,4}.

3. The CCSD valence correlation contribution to the total atomization energy is obtained using the aug-cc-pVQZ + 2d1f and aug-cc-pV5Z + 2d1f basis sets, then extrapolated to the infinite basis limit.

4. The contribution of connected triple excitations is obtained at the CCSD(T) level.

5. The inner-shell correlation contribution is computed as the difference between CCSD(T)/MTsmall values with and without constraining the inner-shell orbitals to be doubly occupied.

6. The scalar relativistic contribution is computed as expectation values of the one-electron Darwin and mass-velocity operators for the ACPF/MTsmall wave function, with all inner-shell electrons correlated except the (1s)-like orbitals of second-row elements.

7. For closed-shell systems, or open-shell systems in nondegenerate electronic states, there is no molecular first-order spin-orbit contribution, and the contribution to total atomization energy is the sum of the atomic spin-orbit corrections.

8. The molecular zero-point energy and thermal corrections were obtained at the B3LYP/cc-pVTZ + 1 level. The zero-point energies within the harmonic approximation are scaled by 0.985.

Table S1. Experimental Adiabatic Ionization Energies (AIEs) for the Compounds Under Consideration

compound	*expt. AIE*/eV
chlorotrifluoromethane	12.6±0.4 [1]
cyanogen chloride	12.36±0.02 [1]
difluorodichloromethane	12.0±0.2 [1]
phosgene	11.7,[2] 11.55±0.02,[3] ~11.2 [4]
fluorotrichloromethane	11.68±0.13 [1]
tetrachloromethane	11.47±0.01 [1]
carbonic difluoride	13.04±0.03 [1]
trichloromethane	11.37±0.02 [1]
trifluoromethane	13.86 [1]
hydrogen cyanide	13.60±0.01 [1]
dichloromethane	11.33±0.04 [1]
difluoromethane	12.71 [1]
formaldehyde	10.88±0.01 [1]
formic acid	11.33±0.01 [1]
chloromethane	11.26±0.03 [1]
methanethiol	9.439±0.005 [1]
methylamine	8.9±0.1 [1]
carbon monoxide	14.014±0.0003 [1]
carbon dioxide	13.777±0.001 [1]
carbon disulfide	10.073±0.005 [1]
chlorotrifluoroethene	9.81±0.03 [1]
tetrachloroethene	9.326±0.001 [1]
tetrafluoroethene	10.14±0.07 [1]
trichloroethene	9.46±0.02 [1]

trichloroacetaldehyde	10.9 [5]
trifluoroethene	10.14 [1]
acetylene	11.400±0.002 [1]
1,1-dichloroethene	9.81±0.04 [1]
cis-1,2-dichloroethene	9.66±0.01 [1]
trans-1,2-dichloroethene	9.64±0.02 [1]
1,1-difluoroethene	10.29±0.01 [1]
chloroethene	9.99±0.02 [1]
fluoroethene	10.36±0.01 [1]
1,1,1-trifluoroethane	13.3±0.1 [6]
acetaldehyde	10.2290±0.0007 [1]
ethylene oxide	10.56±0.01 [1]
acetic acid	10.65±0.02 [1]
dimethyl sulfoxide	9.9±0.1,[7] 9.20±0.05,[8] 9.08±0.09,[9] 9.10 [10]
propene	9.73±0.01 [1]
oxetane	9.65±0.01 [1]
propylene oxide	10.22±0.02 [1]
pyrazine	9.29±0.03,[11] 9.29±0.01,[12] 9.36,[13] 9.28±0.05,[14] 9.216,[15] 9.29,[16] 9.28±0.01,[17] 9.0 [18]
pyrimidine	9.33±0.07 [1]
pyridazine	8.74±0.11 [1]
furan	8.88±0.01 [1]
diketene	9.6±0.02 [19]
thiophene	8.86±0.02 [1]
pyrrole	8.207±0.005 [1]
cyclobutene	9.43±0.02 [1]

bicyclo[1.1.0]butane	8.70±0.01 [1]
cis-2-butene	9.11±0.01 [1]
trans-2-butene	9.10±0.01 [1]
2-methyl-1-propene	9.22±0.02 [1]
tetrahydrofuran	9.40±0.02 [1]
1,3-cyclopentadiene	8.57±0.01 [1]
2-methyl-1-buten-3-yne	9.25±0.02 [1]
cyclopropylacetylene	8.7 [20]
bicyclo[2.1.0]pent-2-ene	8.0 [21]
spiropentane	9.26 [1]
bicyclo[2.1.0]pentane	8.7±0.1 [22]
pentane	10.28±0.10 [1]
isopentane	10.32±0.05 [1]
neopentane	≤10.30±0.08 [1]
benzene	9.24378±0.00007 [1]
3,4-dimethylenecyclobut-1-ene	8.80,[23] 8.80±0.02 [22]
tris(methylene)cyclopropane	9.0±0.1 [24]
phenol	8.49±0.02 [1]
aniline	7.720±0.002 [1]
2-methylpyridine	9.02±0.03,[25] 9.4±0.1,[26] 9.37±0.05 [27]
hexane	10.13±0.10 [1]
toluene	8.828±0.001 [1]
2,5-norbornadiene	8.38±0.04 [1]
quadricyclane	8.70,[28] 7.8 [29]
spiro[2,4]hepta-4,6-diene	8.14 [30]

3-methylenecyclopentene	8.40 [31]
phenylacetylene	8.815±0.005,[25] 8.75,[32] 8.9,[33] 8.82±0.08,[34] 8.825±0.001,[35]
bicyclo[4.2.0]octa-1,3,5-triene	8.74 ± 0.05 [36]
bicyclo[3.2.1]octa-2,6-diene	8.44±0.01 [37]
1-propynylbenzene	8.42±0.08 [34]
1,2,4-trichlorobenzene	9.04±0.03 [38]
o-dichlorobenzene	9.06±0.02 [1]
m-dichlorobenzene	9.10±0.02 [1]
p-dichlorobenzene	8.92±0.03 [1]
o-difluorobenzene	9.29±0.01 [1]
m-difluorobenzene	9.33±0.02 [1]
p-difluorobenzene	9.1589±0.0005 [1]
chlorobenzene	9.07±0.02 [1]
1-buten-3-yne	9.58±0.02 [1]
(Z)-3-penten-1-yne	9.11±0.01 [39]
(Z)-hexa-1,5-diyne-3-ene	9.10±0.02 [22, 40]
(E)-hexa-1,5-diyne-3-ene	9.07±0.02 [22, 40]
1,1-diethynylcyclopropane	8.9 [41]
bicyclo[3.2.0]hepta-2,6-diene	8.35 [42]
3-methylene-1,4-cyclohexadiene	8.6±0.1 [43]
2-norbornene	9.05,[44] 8.95±0.15,[45] 9.0±0.1,[46] 8.83,[47] 8.81±0.02,[37] 8.82,[48] 8.80±0.01,[49] 8.6 [50]
5,5-dimethyl-1,3-cyclopentadiene	8.22±0.05,[52] 8.2 [53]
styrene	8.464±0.001 [1]
2,5-dihydrothiophene	8.4 [54]
carbon suboxide	10.60±0.03,[55] 10.60,[56] 10.605 [57]

4-methylene-2-oxetanone	9.6±0.02 [19]
2-propenenitrile	10.91±0.01 [1]
1H-imidazole	8.81±0.01 [1]
1H-pyrazole	9.27±0.05,[58] 9.25±0.01,[59] 9.38±0.03 [60]
2-butynedinitrile	11.4±0.2,[61] 11.81±0.01,[62] 11.81±0.02 [63]
2,3-diazabicyclo[2.2.1]hept-2-ene	8.45±0.04 [64]
cyclobutadiene	8.5,[65] 8.2,[66] 9.55,[67] 8.16±0.03 [68]
1,2,3-butatriene	9.4,[66] 9.15,[69] 9.15±0.02,[22] 9.25±0.05 [70]
methylenecyclopropene	8.15±0.03 [71]
penta-1,4-diyne	10.27±0.02,[22] 10.1 [72]
1,2,3,4-pentatetraene	8.67±0.02 [22] 8.67 [73]
1-penten-3-yne	9.00±0.01 [1]
hex-3-en-1,5-diyne	9.6±0.2 [74]
bicyclo[2.2.0]hexa-2,5-diene	9.0±0.1 [22]
1-methyl-1,3-cyclopentadiene	8.40±0.02 [1]
5-methyl-1,3-cyclopentadiene	8.45±0.02 [22]
bicyclo[2.2.0]hex-2-ene	9.0±0.1 [22]
1,3-bis(methylene)cyclobutane	8.7 [75]
5-ethenylidene-1,3-cyclopentadiene	8.88 [76]
trans-1,2-diethynylcyclopropane	9.00±0.02 [40]
cis-1,2-diethynylcyclopropane	8.90±0.02 [40]
5-methylenebicyclo[2.2.0]hex-2-ene	8.8 [77]
spiro[3.3]hepta-2,5-diene	9.02 [47]
tricyclo[4.1.0.0^{1,3}]heptane	8.6 [78]
tricyclo[3.1.1.0^{3,6}]heptane	8.7 [79]

1-methyl-1,2-propadienylcyclopropane	8.83 [80]
bicyclo[4.2.0]octa-1,3,5,7-tetraene	7.5 [81]
2,4,6-octatriyne	8.60±0.01, [62] 8.60 [82]
(1α,2β,5β,6α)-tricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene	8.27±0.10 [36]
bicyclo[2.2.2]octa-2,5,7-triene	7.95±0.10,[36] 8.24,[47] 8.23 [83]
pentacyclo[3.3.0.$0^{2,4}$.$0^{3,7}$.$0^{6,8}$]octane	8.18 [84]
7-methylenebicyclo[2.2.1]hepta-2,5-diene	8.5 [85]
tricyclo[4.1.1.$0^{7,8}$]octa-2,4-diene	7.9 [86]
cycloocta-1,5-dien-3-yne	8.2 [87]
cycloocta-1,3-dien-6-yne	8.5 [87]
1,5-dihydropentalene	7.86 [88]
tetrakis(methylene)cyclobutane	8.35 [89]
1,5-dimethyl-3-exo-methylenetricyclo[2.1.0.0]pentane	8.0 [90]
tricyclo[4.1.1.$0^{7,8}$]oct-3-ene	8.3 [86]
tricyclo[4.1.1.$0^{7,8}$]oct-2-ene	8.2 [86]
thieno[3,2-b]thiophene	8.10 [91]
benzodithiete	8.15 [92]
methyloxirane	10.22±0.02 [1]
1,4-dioxin	7.75±0.02 [93]
1,2,4-triazine	9.2 [94]
1-azetine	9.30 [95, 96]
dimethylcyanamide	9.0 [97]
azetidine	9.1±0.15,[98] 8.9,[99] 8.3,[100] 8.63±0.02 [101]
1-methylaziridine	8.7 [100]
3-methyl-1,2,4-triazine	8.6 [94]

2,5-dihydro-1H-pyrrole	8.0 [102]
pyrrole-2-carbonitrile	8.7 [103]
1-methylcyclopropanecarbonitrile	10.53±0.03 [104]

Table S2. Gas Phase (298.15 K, 101.325 kPa) Molecular Enthalpies ($H°_{(g)}$) and Free Energies ($G°_{(g)}$) at the G4 Level of Theory for the Neutral and Cationic Forms of the Compounds Under Consideration

name	*neutral* $H°_{(g)}$/hartree	*cationic* $H°_{(g)}$/hartree	*neutral* $G°_{(g)}$/hartree	*cationic* $G°_{(g)}$/hartree
(1α,2β,5β,6α)-tricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene	-309.313783	-308.994739	-309.350243	-309.033101
(1α,4α,5β)-5-methyl-2-methylenebicyclo[2.1.0]pentane	-272.455465	-272.195210	-272.493812	-272.235276
(E)-hexa-1,5-diyne-3-ene	-230.756440	-230.422836	-230.793328	-230.460582
(Z)-3-penten-1-yne	-193.919293	-193.584577	-193.954775	-193.621035
(Z)-hexa-1,5-diyne-3-ene	-230.756203	-230.421588	-230.793139	-230.459342
1-azetine	-171.902340	-171.560064	-171.932536	-171.591087
1-buten-3-yne	-154.636915	-154.283849	-154.668472	-154.316308
1-methyl-1,2-propadienylcyclopropane	-272.464375	-272.160073	-272.505548	-272.203822
1-methyl-1,3-cyclopentadiene	-233.246869	-232.946816	-233.282510	-232.984121
1-methyl-3-aminopyrazole	-320.684591	-320.406705	-320.723360	-320.445524
1-methyl-5-aminopyrazole	-320.681216	-320.397406	-320.719753	-320.436028
1-methylaziridine	-173.094002	-172.775482	-173.125743	-172.809869
1-methylcyclobutene	-195.134505	-194.806637	-195.168838	-194.844262
1-methylcyclopropanecarbonitrile	-249.291766	-248.927385	-249.328349	-248.966276
1-methylcyclopropene	-155.819675	-155.484837	-155.852055	-155.520167
1-methylnorbornadiene	-310.581891	-310.277342	-310.619295	-310.315902
1-methyltricyclo[4.1.0.$0^{2,7}$]hept-3-ene	-310.554280	-310.257179	-310.592820	-310.297579
1-penten-3-yne	-193.921213	-193.590380	-193.959942	-193.629049
1-propynylbenzene	-347.493270	-347.183535	-347.537918	-347.228517
1-pyrazoline	-227.240441	-226.912598	-227.273753	-226.946747
1,1-dichloroethene	-997.490468	-997.131048	-997.523856	-997.165319
1,1-dicyanoethane	-264.164372	-263.711502	-264.201375	-263.750359
1,1-diethynylcyclopropane	-270.017605	-269.688816	-270.056517	-269.729625
1,1-difluoroethene	-276.972019	-276.594460	-277.002760	-276.626194

1,1-dimethyl-2-methylenecyclopropane	-234.400626	-234.076006	-234.438783	-234.117150
1,1,1-trifluoroethane	-377.440160	-376.981472	-377.473833	-377.017826
1,1'-biaziridine	-266.442968	-266.147921	-266.479024	-266.184793
1,2-bis(methylene)cyclobutane	-233.204871	-232.886100	-233.241660	-232.923608
1,2-dimethylcyclopropene	-195.104510	-194.788578	-195.141078	-194.827595
1,2,3-butatriene	-154.624604	-154.287823	-154.656255	-154.320408
1,2,3,4-pentatetraene	-192.681356	-192.359006	-192.715623	-192.394187
1,2,4-triazine	-280.186959	-279.853104	-280.219487	-279.886187
1,2,4-trichlorobenzene	-1610.551639	-1610.221968	-1610.594666	-1610.265978
1,3-bis(methylene)cyclobutane	-233.200851	-232.866197	-233.237906	-232.904196
1,3-cyclopentadiene	-193.964214	-193.648428	-193.995967	-193.681130
1,3-dimethylbicyclo[1.1.0]butane	-234.390698	-234.099053	-234.428327	-234.138412
1,3-dioxol-2-one	-341.043553	-340.689113	-341.075779	-340.722150
1,4-dioxin	-305.054476	-304.765900	-305.088775	-304.799641
1,5-dihydropentalene	-309.405498	-309.116775	-309.442360	-309.154546
1,5-dimethyl-3-exo-methylenetricyclo[2.1.0.0]pentane	-310.498584	-310.217500	-310.540074	-310.260871
1H-imidazole	-226.095337	-225.771377	-226.126353	-225.803167
1H-pyrazole	-226.077839	-225.736973	-226.108828	-225.769083
2-(1,1-dimethylethyl)thiirane	-633.713836	-633.397831	-633.756471	-633.441695
2-aziridinecarbonitrile	-226.042740	-225.667248	-226.075759	-225.701690
2-butynedinitrile	-261.719903	-261.280924	-261.753031	-261.315102
2-methyl-1-buten-3-yne	-193.919374	-193.579285	-193.954630	-193.616884
2-methyl-1-propene	-157.081679	-156.741944	-157.115313	-156.778118
2-methyl-1,3-dithiacyclopentane	-953.244311	-952.929204	-953.284154	-952.969277
2-methyl-1,5-diazabicyclo[3.1.0]hexane	-305.764932	-305.475052	-305.803099	-305.513944

2-methyl-1H-imidazole	-265.380503	-265.072859	-265.415909	-265.109612
2-methylpyridine	-287.416758	-287.085717	-287.454220	-287.124894
2-methylthietane	-555.149239	-554.836355	-555.185103	-554.873495
2-norbornene	-272.523120	-272.199539	-272.557939	-272.236401
2-propenenitrile	-170.740978	-170.338306	-170.771963	-170.370544
2-pyrazoline	-227.242178	-226.944651	-227.274445	-226.977777
2,2-dimethylthiirane	-555.158256	-554.839841	-555.194476	-554.877640
2,3-bis(methylene)bicyclo[2.2.0]hexane	-310.541964	-310.228960	-310.581977	-310.270153
2,3-diazabicyclo[2.2.1]-hept-2-ene	-304.604893	-304.291070	-304.639401	-304.327101
2,3-dihydrothiophene	-553.963749	-553.669601	-553.997732	-553.704516
2,4,6-octatriyne	-308.103310	-307.789680	-308.149763	-307.836823
2,5-dihydro-1H-pyrrole	-211.200403	-210.903287	-211.233608	-210.936654
2,5-dihydrofuran	-231.072901	-230.734590	-231.105743	-230.767688
2,5-dihydrothiophene	-553.962859	-553.650770	-553.997135	-553.685385
2,5-norbornadiene	-271.298869	-270.990482	-271.332908	-271.025580
2(3H)-furanone	-305.118140	-304.777183	-305.151909	-304.812455
2a,2b,4a,4b-tetrahydrocyclopropa[cd]pentalene	-309.379279	-309.076615	-309.414664	-309.114445
3-(cis-ethylidene)-1-cyclopentene	-272.521233	-272.229441	-272.561541	-272.269713
3-methyl-1,2-dithiolane	-953.247290	-952.965811	-953.287494	-953.005630
3-methyl-1,2,4-triazine	-319.474318	-319.152003	-319.511215	-319.189931
3-methylene-1,4-cyclohexadiene	-271.325632	-271.027367	-271.362151	-271.064740
3-methylenecyclopentene	-233.242167	-232.936237	-233.278046	-232.972397
3-methyleneoxetane	-231.040969	-230.692061	-231.074469	-230.726370
3-methylenetetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane	-309.331510	-309.046755	-309.367358	-309.083933
3-methylthietane	-555.148155	-554.834523	-555.184038	-554.871389

3,3-dimethylcyclobutene	-234.412531	-234.073137	-234.449453	-234.113651
3,3-dimethyldiaziridine	-228.417315	-228.092218	-228.452247	-228.128609
3,3-dimethylthietane	-594.431670	-594.120445	-594.470392	-594.160360
3,4-dimethylenecyclobut-1-ene	-231.991811	-231.668364	-232.026928	-231.704539
3,6-bis(methylene)-1,4-cyclohexadiene	-309.410135	-309.122067	-309.448499	-309.161198
3(2H)-furanone	-305.101988	-304.751455	-305.135845	-304.785787
4-aminopyrimidine	-319.525431	-319.196280	-319.561001	-319.232718
4-methyl-1,2-dithiolane	-953.245948	-952.963870	-953.285703	-953.003545
4-methyl-1,3-dithiolane	-953.243635	-952.929076	-953.283791	-952.969202
4-methyl-3H-1,2-dithiole-3-thione	-1348.940717	-1348.640007	-1348.981743	-1348.682010
4-methylene-1,3-dioxolane	-306.272650	-305.953387	-306.307885	-305.989252
4-methylene-2-oxetanone	-305.096107	-304.752748	-305.130713	-304.789713
5-(dimethylamino)tetrazole	-392.020939	-391.706806	-392.062352	-391.749208
5-ethenylidene-1,3-cyclopentadiene	-270.091126	-269.788724	-270.127903	-269.826330
5-methyl-1,3-cyclopentadiene	-233.242316	-232.931205	-233.277476	-232.967577
5-methylenebicyclo[2.2.0]hex-2-ene	-271.255116	-270.931864	-271.291596	-270.969194
5-methylenebicyclo[2.2.1]hept-2-ene	-310.587845	-310.272572	-310.625225	-310.311594
5,5-dimethyl-1,3-cyclopentadiene	-272.523274	-272.216562	-272.561466	-272.256199
5,5-dimethylbicyclo[2.1.0]pent-2-ene	-272.453440	-272.164061	-272.491355	-272.203806
6-methylfulvene	-271.320803	-271.023068	-271.358562	-271.061651
7-methylenebicyclo[2.2.1]hepta-2,5-diene	-309.363925	-309.054907	-309.400449	-309.092936
7-methylenebicyclo[3.2.0]hept-1-ene	-310.557924	-310.254091	-310.596771	-310.294137
7-thiabicyclo[4.1.0]heptane	-632.483093	-632.170141	-632.520830	-632.209440
acetaldehyde	-153.738936	-153.362949	-153.768704	-153.393723
acetic acid	-228.977339	-228.587089	-229.010208	-228.620361

acetylene	-77.286490	-76.867092	-77.310021	-76.891141
aniline	-287.420475	-287.136030	-287.456468	-287.172576
anti-tricyclo[3.2.0.0^{2,4}]hept-6-ene	-271.247649	-270.930602	-271.282467	-270.967230
anti-tricyclo[3.2.0.0^{2,4}]heptane	-272.463436	-272.151741	-272.499357	-272.189416
anti-tricyclo[4.2.0.0^{2,5}]octane	-311.740515	-311.431751	-311.779454	-311.472806
azetidine	-173.101691	-172.795857	-173.132735	-172.828301
benzene	-232.088591	-231.747271	-232.121477	-231.782275
benzodithiete	-1027.031609	-1026.725713	-1027.070145	-1026.765416
bicyclo[1.1.0]but-1(3)-ene	-154.531212	-154.194721	-154.561321	-154.225722
bicyclo[1.1.0]butane	-155.826121	-155.503257	-155.856284	-155.534337
bicyclo[1.1.0]butane-1-carbonitrile	-248.051580	-247.704671	-248.086341	-247.740595
bicyclo[2.1.0]pent-2-ene	-193.890896	-193.591315	-193.922470	-193.624327
bicyclo[2.1.0]pentane	-195.120503	-194.802300	-195.152796	-194.836423
bicyclo[2.1.0]pentane-1-carbonitrile	-287.348595	-287.008428	-287.385464	-287.047537
bicyclo[2.1.1]hex-2-ene	-233.197671	-232.882255	-233.230466	-232.916350
bicyclo[2.2.0]hex-2-ene	-233.185762	-232.858727	-233.219825	-232.895270
bicyclo[2.2.0]hexa-2,5-diene	-231.967026	-231.638673	-232.000049	-231.672910
bicyclo[2.2.2]octa-2,5,7-triene	-309.382194	-309.079760	-309.417681	-309.116619
bicyclo[3.2.0]hept-1-ene	-272.488875	-272.182868	-272.525364	-272.221046
bicyclo[3.2.0]hept-1(5)-ene	-272.484139	-272.175394	-272.521851	-272.214905
bicyclo[3.2.0]hepta-1,4,6-triene	-270.055800	-269.741030	-270.090642	-269.777168
bicyclo[3.2.0]hepta-2,6-diene	-271.289964	-270.971008	-271.325348	-271.007361
bicyclo[3.2.1]octa-2,6-diene	-310.602636	-310.296733	-310.639110	-310.334182
bicyclo[3.3.0]octa-2,6-diene	-310.609084	-310.277948	-310.646974	-310.317778
bicyclo[4.1.0]hepta-1,3,5-triene	-270.081134	-269.757400	-270.116099	-269.793576

bicyclo[4.2.0]octa-1,3,5-triene	-309.418432	-309.099653	-309.455309	-309.138190
bicyclo[4.2.0]octa-1,3,5,7-tetraene	-308.174843	-307.889753	-308.211060	-307.926823
carbon dioxide	-188.531709	-188.025435	-188.555960	-188.051242
carbon disulfide	-834.231249	-833.859726	-834.258202	-833.887572
carbon monoxide	-113.286121	-112.769686	-113.308553	-112.792746
carbon suboxide	-264.624653	-264.233024	-264.656040	-264.265469
carbonic difluoride	-312.939353	-312.463028	-312.969405	-312.493902
chlorobenzene	-691.578041	-691.244137	-691.613709	-691.280990
chloroethene	-538.006038	-537.639449	-538.036004	-537.670316
chloromethane	-499.940833	-499.526969	-499.968484	-499.556047
chlorotrifluoroethene	-835.659605	-835.301090	-835.696201	-835.338369
chlorotrifluoromethane	-797.631741	-797.175337	-797.665285	-797.212792
cis-1,2-dichloroethene	-997.491299	-997.138260	-997.524876	-997.172565
cis-1,2-diethynylcyclopropane	-270.018547	-269.690699	-270.057548	-269.731711
cis-2-butene	-157.077201	-156.741126	-157.111508	-156.777673
cyanogen chloride	-552.865765	-552.412619	-552.887389	-552.434398
cyclobutadiene	-154.583532	-154.287356	-154.613610	-154.318221
cyclobutane-1,3-dione	-305.092192	-304.735401	-305.127983	-304.771864
cyclobutene	-155.849212	-155.501233	-155.879637	-155.533496
cycloocta-1,3-dien-6-yne	-309.328607	-309.012455	-309.368020	-309.053161
cycloocta-1,5-dien-3-yne	-309.341857	-309.034208	-309.380272	-309.074575
cyclopentyl acetylene	-272.489813	-272.134905	-272.530572	-272.175738
cyclopropanimine	-171.890823	-171.567297	-171.921775	-171.600153
cyclopropylacetylene	-193.903271	-193.565399	-193.937137	-193.603660
cyclopropylidenemethanone	-229.844397	-229.522827	-229.878974	-229.557574

dichloromethane	-959.421970	-959.013878	-959.453358	-959.045942
difluorodichloromethane	-1157.875761	-1157.444671	-1157.910741	-1157.480715
difluoromethane	-238.906193	-238.437271	-238.934842	-238.466662
dihydro-2(3H)-thiophenthione	-952.053441	-951.748257	-952.090938	-951.786527
diketene	-305.096107	-304.752748	-305.130713	-304.789713
dimethyl sulfoxide	-552.979400	-552.653946	-553.014433	-552.690494
dimethylcyanamide	-227.255951	-226.918008	-227.292115	-226.956294
dithio-p-benzoquinone	-1027.006964	-1026.685560	-1027.046434	-1026.726017
endo-2-methylene-5-methylbicyclo[2.1.0]pentane	-272.470146	-272.174590	-272.508316	-272.214123
ethylene oxide	-153.696203	-153.307504	-153.724403	-153.336908
ethylidenecyclopropane	-195.118534	-194.786951	-195.153737	-194.823865
ethynylcyclobutane	-233.183432	-232.833359	-233.219902	-232.871685
fluoroethene	-177.742280	-177.361815	-177.770936	-177.391483
fluorotrichloromethane	-1518.124129	-1517.694564	-1518.160490	-1517.734431
formaldehyde	-114.449376	-114.049116	-114.474845	-114.075353
formic acid	-189.688872	-189.273643	-189.717070	-189.302660
furan	-229.897932	-229.571166	-229.928908	-229.603003
heptafulvene	-309.393342	-309.117955	-309.431858	-309.156890
hex-3-en-1,5-diyne	-230.756440	-230.422835	-230.793329	-230.460582
hexane	-236.840848	-236.473346	-236.882927	-236.517586
hydrogen cyanide	-93.389268	-92.888925	-93.412097	-92.912723
isopentane	-197.566343	-197.198098	-197.604462	-197.239313
m-dichlorobenzene	-1151.066452	-1150.730965	-1151.106202	-1150.771823
m-difluorobenzene	-430.538115	-430.194986	-430.575191	-430.233288
methanethiol	-438.524737	-438.177621	-438.553546	-438.207247

methylamine	-95.773933	-95.441248	-95.801226	-95.470921
methylenecyclopropene	-154.599350	-154.300448	-154.629952	-154.332357
methylmethylenecyclopropane	-195.117971	-194.778990	-195.152925	-194.816170
methyloxirane	-192.980657	-192.609697	-193.012457	-192.643419
N-methylazetidine	-212.376216	-212.089173	-212.410597	-212.126738
neopentane	-197.572420	-197.198384	-197.609773	-197.238899
norbornan-7-one	-347.746566	-347.423461	-347.784673	-347.463244
o-dichlorobenzene	-1151.064134	-1150.731573	-1151.103741	-1150.772326
o-difluorobenzene	-430.532097	-430.190495	-430.569229	-430.228815
oxetane	-192.974908	-192.618800	-193.006716	-192.650933
p-dichlorobenzene	-1151.066179	-1150.738666	-1151.105931	-1150.779403
p-difluorobenzene	-430.536846	-430.200653	-430.573286	-430.238215
penta-1,4-diyne	-192.678813	-192.299814	-192.713503	-192.335258
pentacyclo[3.3.0.$0^{2,4}$.$0^{3,7}$.$0^{6,8}$]octane	-309.325241	-309.022025	-309.359237	-309.057826
pentane	-197.563941	-197.188626	-197.602416	-197.230388
phenol	-307.293306	-306.979993	-307.328817	-307.016316
phenylacetylene	-308.208840	-307.883807	-308.246879	-307.922974
phosgene	-1033.444690	-1033.022071	-1033.477588	-1033.056083
propene	-117.798825	-117.439781	-117.828893	-117.472715
propylene oxide	-192.980657	-192.604222	-193.012456	-192.637860
pyrazine	-264.171963	-263.830872	-264.204481	-263.864442
pyridazine	-264.143583	-263.823826	-264.176203	-263.857125
pyrimidine	-264.179006	-263.833967	-264.211549	-263.867316
pyrrole	-210.039125	-209.737137	-210.070501	-209.769200
pyrrole-2-carbonitrile	-302.264369	-301.938593	-302.300230	-301.975369

quadricyclane	-271.262749	-270.981211	-271.296266	-271.015956
spiro[2,4]hepta-4,6-diene	-271.303503	-271.005390	-271.339672	-271.042626
spiro[3.3]hepta-2,5-diene	-271.250835	-270.919768	-271.287494	-270.958165
spiropentane	-195.110067	-194.764940	-195.143398	-194.800813
styrene	-309.437701	-309.125540	-309.477096	-309.165128
syn-tricyclo[3.2.0.$0^{2,4}$]heptane	-272.449013	-272.153369	-272.484425	-272.190622
tetrachloroethene	-1916.454495	-1916.114915	-1916.494644	-1916.155735
tetrachloromethane	-1878.377674	-1877.953891	-1878.415362	-1877.994630
tetracyclo[4.1.0.$0^{2,4}$.$0^{3,5}$]heptane	-271.249970	-270.940972	-271.284093	-270.976672
tetrafluoroethene	-475.396249	-475.026820	-475.431663	-475.062953
tetrahydrofuran	-232.282037	-231.935668	-232.316901	-231.969891
tetrakis(methylene)cyclobutane	-309.347513	-309.040532	-309.388278	-309.082160
thieno[3,2-b]thiophene	-1027.045305	-1026.747133	-1027.083456	-1026.786033
thieno[3,4-b]thiophene	-1027.038097	-1026.748356	-1027.076232	-1026.787222
thiophene	-552.787918	-552.461146	-552.820212	-552.494532
toluene	-271.370144	-271.044533	-271.408425	-271.084210
trans-1,2-dichloroethene	-997.490320	-997.138504	-997.524000	-997.172909
trans-1,2-diethynylcyclopropane	-270.020028	-269.693348	-270.059101	-269.734084
trans-2-butene	-157.079268	-156.743018	-157.113126	-156.778949
trans-2,3,4-hexatriene	-233.185978	-232.880288	-233.225898	-232.921586
trichloroacetaldehyde	-1532.180940	-1531.800189	-1532.220688	-1531.842713
trichloroethene	-1456.973679	-1456.627900	-1457.010627	-1456.665536
trichloromethane	-1418.901777	-1418.482050	-1418.936495	-1418.518987
tricyclo[3.1.0.$0^{2,6}$]hexane	-233.198041	-232.878420	-233.231330	-232.913061
tricyclo[3.1.1.$0^{3,6}$]heptane	-272.465264	-272.145097	-272.500059	-272.181798

tricyclo[4.1.0.0^{1,3}]heptane	-272.462325	-272.148452	-272.498456	-272.186498
tricyclo[4.1.0.0^{2,4}]heptane	-272.494982	-272.171402	-272.530542	-272.209206
tricyclo[4.1.0.0^{2,7}]hept-3-ene	-271.271148	-270.964174	-271.305986	-271.000350
tricyclo[4.1.0.0^{2,7}]heptane	-272.479552	-272.172802	-272.515104	-272.209586
tricyclo[4.1.1.0^{7,8}]oct-2-ene	-310.542627	-310.239668	-310.580214	-310.278437
tricyclo[4.1.1.0^{7,8}]oct-3-ene	-310.542144	-310.233132	-310.580001	-310.272505
tricyclo[4.1.1.0^{7,8}]octa-2,4-diene	-309.339613	-309.043042	-309.376221	-309.083332
trifluoroethene	-376.178897	-375.807836	-376.212119	-375.841855
trifluoromethane	-338.150206	-337.644035	-338.180739	-337.675467
trimethylthiirane	-594.439069	-594.127310	-594.478768	-594.168702
tris(methylene)cyclopropane	-231.953138	-231.619433	-231.989485	-231.658392
α-trimethylethylene oxide	-271.548973	-271.208187	-271.587915	-271.250146

Table S3. Gas Phase (298.15 K, 101.325 kPa) Molecular Enthalpies ($H°_{(g)}$) and Free Energies ($G°_{(g)}$) at the W1BD Level of Theory for the Neutral and Cationic Forms of the Compounds Under Consideration

name	*neutral* $H°_{(g)}$/hartree	*cationic* $H°_{(g)}$/hartree	*neutral* $G°_{(g)}$/hartree	*cationic* $G°_{(g)}$/hartree
acetaldehyde	-153.837683	-153.460711	-153.867478	-153.491477
acetylene	-77.321361	-76.902255	-77.344738	-76.926307
carbon dioxide	-188.681389	-188.172739	-188.705656	-188.198588
carbon monoxide	-113.369249	-112.853344	-113.391673	-112.876394
carbonic difluoride	-313.239113	-312.760041	-313.269192	-312.790915
chloroethene	-539.460248	-539.091895	-539.490198	-539.122741
chloromethane	-501.376575	-500.961367	-501.404223	-500.990345
cyanogen chloride	-554.339285	-553.883091	-554.360746	-553.910553
difluoromethane	-239.137702	-238.668328	-239.166381	-238.697723
ethylene oxide	-153.794731	-153.405173	-153.822936	-153.434586
fluoroethene	-177.884296	-177.503214	-177.912959	-177.532879
formaldehyde	-114.530727	-114.129869	-114.556193	-114.156098
formic acid	-189.837549	-189.420587	-189.865756	-189.449598
hydrogen cyanide	-93.443083	-92.942563	-93.465937	-92.966406
methanethiol	-439.625259	-439.277832	-439.654082	-439.307436
methylamine	-95.825074	-95.491979	-95.852408	-95.521698
propene	-117.848524	-117.489737	-117.878599	-117.523231

References

[1] 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).

[2] Cermak, V. Penning Ionization Electron Spectroscopy. I. Determination of Ionization Potentials of Polyatomic Molecules. *Collection Czech. Chem. Commun*. **1968**, *33*, 2739-2763.

[3] Chadwick, D. Photoelectron Spectra of Phosgene and Thiophosgene. *Can. J. Chem.* **1972**, *50*, 737-746.

[4] Thomas, R. K.; Thompson, H. Photoelectron Sspectra of Carbonyl Halides and Related Compounds. *Proc. R. Soc. London A* **1972**, *327*, 13-22.

[5] Guimon, G.; Pfister-Guillouzo, G.; Rima, G.; El Amine, M.; Barrau, J. Generation, Detection and Electronic Structure of Dimethyl Germanone by Photoelectron Spectroscopy and Quantum Calculations. *Spectrosc. Lett*. **1985**, *18*, 7-14.

[6] Simmie, J. M.; Tschuikow-Roux, E. Mass Spectrum, Appearance Potentials and Bond Dissociation Energies of 1,1,1-Trifluoroethane. *Int. J. Mass Spectrom. Ion Phys.* **1971**, *7*, 41-45.

[7] Blais, J. C.; Cottin, M.; Gitton, B. Ionisation Positive et Negative dans le Dimethylsulfoxyde en Phase Gazeuse. *J. Chim. Phys.* **1970**, *67*, 1475.

[8] Distefano, G.; Foffani, A.; Innorta, G.; Pignataro, S. Electron Impact Ionization Potentials of Some Manganese, Chromium and Tungsten Organometallic Derivatives. *Int. J. Mass Spectrom. Ion Phys.* **1971**, *7*, 383-390.

[9] Potzinger, P.; Stracke, H. U.; Kupper, W.; Gollnick, K. Ionisierungs - und Auftrittspotentialmessungen an Dialkylsulfoxiden. *Z. Naturforsch. A* **1975**, *30*, 340.

[10] 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.

[11] 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. Spect.* **1965**, *15*, 407-434.

[12] Yencha, A. J.; El-Sayed, M. A. Lowest Ionization Potentials of Some Nitrogen Heterocyclics. *J. Chem. Phys.* **1968**, *48*, 3469-3475.

[13] 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.

[14] Eland, J. H. D. Photoelectron Spectra of Conjugated Hydrocarbons and Heteromolecules. *Int. J. Mass Spectrom. Ion Phys.* **1969**, *2*, 471-484.

[15] 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.

[16] 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.

[17] Scheps, R.; Florida, D.; Rice, S. A. Comments on the Rydberg Spectrum of Pyrazine. *J. Mol. Spectr.* **1972**, *44*, 1-13.

[18] 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.

[19] Olivares, J. A.; Flesch, G. D.; Svec, H. J. Mass Spectrometry of Five Ketene Dimers. *Int. J. Mass Spectrom. Ion Processes* **1984**, *56*, 297-305.

[20] Bruckmann, P.; Klessinger, M. Photoelektronenspektren Organischer Verbindungen. III. Photoelektronenspektren Acetylensubstituierter Kleiner Ringe. *J. Electron Spectrosc. Relat. Phenom.* **1973**, *2*, 341-354.

[21] Andrews, G. D.; Baldwin, J. E.; Gilbert, K. E. Photoelectron Spectrum of Bicyclo[2.1.0]pent-2-

ene: Electronic Destabilization of a Homo[4n]annulene. *J. Org. Chem.* **1980**, *45*, 1523-1524.

[22] Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. Valence Ionization Energies of Hydrocarbons. *Helv. Chim. Acta* **1977**, *60*, 2213-2233.

[23] Heilbronner, E.; Gleiter, R.; Hopf, H.; Homung, V.; deMeijere, A. Photoelectron-Spectroscopic Evidence for the Orbital Sequence in Fulvene and 3,4-Dimethylenecyclobutene. *Helv. Chim. Acta* **1971**, *54*, 783.

[24] Dorko, E. A.; Scheps, R.; Rice, S. A. Comments on the Ultraviolet Spectrum and Photophysical Properties of Trimethylenecyclopropane. *J. Phys. Chem.* **1974**, *78*, 568-571.

[25] Watanabe, K.; Nakayama, T.; Mottl, J. Ionization Potentials of Some Molecules. *J. Quant. Spectry. Radiative Transfer* **1962**, *2*, 369-382.

[26] Stefanovic, D.; Grutzmacher, H. F. The Ionisation Potential of Some Substituted Pyridines. *Org. Mass Spectrom.* **1974**, *9*, 1052-1054.

[27] Zaretskii, Z. V. I.; Oren, D.; Kelner, L. Automatic Method for the Measurement of the Electron Impact Ionization and Appearance Potentials. *Appl. Spectrosc.* **1976**, *30*, 366-368.

[28] Dolejsek, Z.; Hanus, V.; Prinzbach, H. Das Massenspektrometrische Verhalten von Quadricyclen. *Angew. Chem.* **1962**, *74*, 902-903.

[29] Martin, H. D.; Heller, C.; Haselbach, E.; Lanyjova, Z. 49. Quadricyclanes. Part I: Photoelectron Spectra and Electronic Structure. *Helv. Chim. Acta* **1974**, *57*, 465-472.

[30] Gleiter, R.; Heilbronner, E.; de Meijere, A. Die Konjugative Wechselwirkung Zwischen π-und Walsh-Orbitalen: Das Photoelektron-Spektrum des Homofulvens. *Helv. Chim. Acta* **1971**, *54*, 1029-1037.

[31] Bruckmann, P.; Klessinger, M. Photoelektronenspektren Organischer Verbindungen. V. Wechselwirkung Kleiner Ringe mit π-Systemen. *Chem. Ber.* **1974**, *107*, 1108-1125.

[32] Rabalais, J. W.; Colton, R. J. Electronic Interaction Between the Phenyl Group and Its Unsaturated

Substituents. J. *Electron Spectrosc. Relat. Phenom.* **1973**, *1*, 83-99.

[33] Koppel, C.; Schwarz, H.; Bohlmann, F. Elektronenstossinduzierte Fragmentierung von Acetylenverbindungen. IX - Struktur der Stabilen $[C_9H_{11}]^+$ - Ionen aus Isomeren C_9H_{11} - Chloriden. *Org. Mass Spectrom.* **1974**, *9*, 321-323.

[34] Elbel, S.; Lienert, K.; Krebs, A.; Dieck, H. T. Phenylethin - Mustersonde fur Substituenteneffekte. *Liebigs Ann. Chem.* **1981**, 1785-1797.

[35] Dyke, J. M.; Ozeki, H.; Takahashi, M.; Cockett, M. C. R.; Kimura, K. A Study of Phenylacetylene and Styrene, and Their Argon Complexes PA-Ar and ST-Ar with Laser Threshold Photoelectron Spectroscopy. *J. Chem. Phys.* **1992**, *97*, 8926-8933.

[36] Franklin, J. L.; Carroll, S. R. The Effect of Molecular Structure on Ionic Decomposition. I. An Electron Impact Study of Seven C_8H_8 Isomers. *J. Am. Chem. Soc.* **1969**, *91*, 5940-5946.

[37] Demeo, D. A.; El-Sayed, M. A. Ionization Potential and Structure of Olefins. *J. Chem. Phys.* **1970**, *52*, 2622-2629.

[38] 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).

[39] Carlier, P.; Mouvier, G.; Mesnard, D.; Miginiac, L. Etude par Spectrometrie de Photoelectrons de la Structure Electronique des Phenyl-Alcynes Conjugues. *J. Electron Spectrosc. Relat. Phenom.* **1979**, *16*, 169-181.

[40] Brogli, F.; Heilbronner, E.; Wirz, J.; Kloster-Jensen, E.; Bergman, R. G.; Vollhardt, K. P. C.; Ashe, A. J. The Consequences of σ and π Conjugative Interactions in Mono-, Di- and Triacetylenes. A Photoelectron Spectroscopic Investigation. *Helv. Chim. Acta* **1975**, *58*, 2620-2645.

[41] Eckert-Maksie, M.; Gleiter, R.; Zefirov, N. S.; Kozhushkov, S. I.; Kuznetsova, T. S. Photoelectron

Spectra of Geminal Vinyl- and Ethynyl-Disubstituted Cyclopropane Derivatives. *Chem. Ber.* **1991**, *124*, 371-376.

[42] Traeger, J. C.; McLoughlin, R. G. A Photoionization Study of the Energetics of $C_7H_7^+$ Ion Formed from C_7H_8 Precursors. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *27*, 319-333.

[43] Bartmess, J. E. Gas Phase Ion Chemistry of 5-Methylene-1,3-cyclohexadiene (o-Isotoluene) and 3-Methylene-1,4-cyclohexadiene (p-Isotoluene). *J. Am. Chem. Soc.* **1982**, *104*, 335-337.

[44] Winstein, S.; Lossing, F. P. On the Question of Homoconjugation in 1,4,7-Cyclononatriene. *J. Am. Chem. Soc.* **1964**, *86*, 4485-4486.

[45] Steele, W. C.; Jennings, B. H.; Botyos, G. L.; Dudek, G. O. An Electron Impact Study of Norbornenyl and Nortricyclyl Chlorides. *J. Org. Chem.* **1965**, *30*, 2886-2889.

[46] Muller, J.; Herberhold, M. Massenspektroskopische Untersuchungen an $C_5H_5Mn(CO)_3$ und $C_5H_5Mn(CO)_2$ L-Komplexen. *J. Organometal. Chem.* **1968**, *13*, 399-410.

[47] Bodor, N.; Dewar, M. J.S .; Worley, S. D. Photoelectron Spectra of Molecules. III. Ionization Potentials of Some Cyclic Hydrocarbons and Their Derivatives, and Heats of Formation and Ionization Potentials Calculated by the MINDO SCF MO Method. *J. Am. Chem. Soc.* **1970**, *92*, 19-24.

[48] Demeo, D. A.; Yencha, A. J. Photoelectron Spectra of Bicyclic and Exocyclic Olefins. *J. Chem. Phys.* **1970**, *53*, 4536-4533.S

[49] Holmes, J. L.; McGillivray, D. The Mass Spectra of Isomeric Hydrocarbons - I. Norbornene and Nortricyclene; The Mechanisms and Energetics of Their Fragmentations. *Org. Mass Spectrom.* **1971**, *5*, 1349-1362.

[50] Wen, A. T.; Hitchcock, A. P.; Werstiuk, N. H.; Nguyen, N.; Leigh, W. J. Studies of Electronic Excited States of Substituted Norbornenes by UV Absorption, Electron Energy Loss, and HeI Photoelectron Spectroscopy. *Can. J. Chem.* **1990**, *68*, 1967-.

[51] Della, E. W.; Pigou, P. E.; Livett, M. K.; Peel, J. B. The Photoelectron Spectrum of 1-

Bromotricyclene. *Aust. J. Chem.* **1985**, *38*, 69.

[52] Meyer, F.; Harrison, A. G. Ionization Potentials of Methyl-Substituted Benzenes and Cyclopentadienes. *Can. J. Chem.* **1964**, *42*, 2256-2261.

[53] Guimon, C.; Pfister-Guillouzo, G.; Dubac, J.; Laporterie, A.; Manuel, G.; Iloughmane, H. Electronic Structure of Group 14 (η_4-Metallole)tricarbonyliron Complexes. *Organometallics* **1985**, *4*, 636-641.

[54] Schmidt, H.; Schweig, A. Ausschluss Transanularer Wechselwirkung in 2,5-Dihydrothiophen. *Tetrahedron Lett.* **1973**, 1437-1440.

[55] Kim, H. H.; Roebber, J. L. Vacuum-Ultraviolet Absorption Spectrum of Carbon Suboxide. *J. Chem. Phys.* **1966**, *44*, 1709-1710.

[56] Baker, C.; Turner, D. W. The Photoelectron Spectrum and Ionisation Potentials of Carbon Cuboxide. *Chem. Commun.* **1969**, 400.

[57] Rabalais, J. W.; Bergmark, T.; Werme, L. O.; Karlson, L.; Hussain, M.; Siebahn, K. *Electron Spectroscopy*. North-Holland Publishing Company: Amsterdam, NL, 1972.

[58] Baker, A.D.; Betteridge, D.; Kemp, N. R.; Kirby, R. E. Application of Photoelectron Spectrometry to Pesticide Analysis. Photoelectron Spectra of Five-membered Heterocycles and Related Molecules. *Anal. Chem.* **1970**, *42*, 1064-1073.

[59] Main-Bobo, J.; Loesik, S.; Gase, W.; Baer, T.; Mommers, A.; Holmes, J. The Thermochemistry and Dissociation Dynamics of Internal-Energy Selected Pyrazole and Imidazole Ions. *J. Am. Chem. Soc.* **1986**, *108*, 677-683.

[60] Lichtenberger, D. L.; Copenhaver, A. S.; Gray, H. B.; Marshall, J. L.; Hopkins, M. D. Valence Electronic Structure of Bis(Pyrazolyl)-Bridged Iridium Dicarbonyl Dimers. Electronic Effects of 3,5-Dimethylpyraxzolyl Substitution on Metal-Metal Interactions. *Inorg. Chem.* **1988**, *27*, 4488.

[61] Dibeler, V. H.; Reese, R. M.; Franklin, J. L. Mass Spectrometric Study of Cyanogen and

Cyanoacetylenes. *J. Am. Chem. Soc.* **1961**, *83*, 1813-1818.

[62] Baker, C.; Turner, D. W. High Resolution Molecular Photoelectron Spectroscopy. III. Acetylenes and Szaacetylenes. *Proc. Roy. Soc. (London)* **1968**, *a308*, 19-37.

[63] Maier, J. P.; Misev, L.; Thommen, F. Dicyanoacetylene Cation. Laser-Induced Fluorescence and Photoelectron-Photon Coincidence Studies. *J. Phys. Chem.* **1982**, *86*, 514-518.

[64] Boyd, R. J.; Bunzli, J. C.; Snyder, J. P.; Heyman, M. L. Photoelectron Spectra of 2,3-Diazabicyclo[2.2n]alk-2-enes (n=1,2,3,4). *J. Am. Chem. Soc.* **1973**, *95*, 6478-6480.

[65] Dewar, M. J. S.; Worley, S. D. Photoelectron Spectra of Molecules. I. Ionization Potentials of Some Organic Molecules and Their Interpretation. *J. Chem. Phys.* **1969**, *50*, 654-657.

[66] Hedaya, E.; Miller, R. D.; McNeil, D. W.; D'Angelo, P. F.; Schissel, P. Flash Vacuum Pyrolysis. V. Cyclobutadiene. *J. Am. Chem. Soc.* **1969**, *91*, 1875-1877.

[67] Li, P. H.; McGee, H. A. Mass Spectrum and Ionization Potential of Condensed Cyclobutadiene. *Chem. Commun.* **1969**, 592.

[68] Kohn, D. W.; Chen, P. Vibrational Structure in the Photoelectron Spectrum of Cyclobutadiene as a Probe of Structure. *J. Am. Chem. Soc.* **1993**, *115*, 2844-2848.

[69] Brogli, F.; Heilbronner, E.; Kloster-Jensen, E.; Schmelzer, A.; Manocha, A. S.; Pople, J. A.; Radom, L. The Photoelectron Spectrum of Butatriene. *Chem. Phys.* **1974**, *4*, 107.

[70] Rosenstock, H. M.; McCulloh, K. E.; Lossing, F. P. On the Mechanisms of C_6H_6 Ionization Fragmentation. *Int. J. Mass Spectrom. Ion Phys.* **1977**, *25*, 327-341.

[71] Staley, S. W.; Norden, T. D. Structure and Energetics of $C_4H_4^+$ in the Gas Phase. Photoelectron Spectrum of Methylenecyclopropene. *J. Am. Chem. Soc.* **1989**, *111*, 445.

[72] Holmes, J. L.; Lossing, F. P. Personal Communication to S.G. Lias. **1986**.

[73] Bieri, G.; Dill, J. D.; Heilbronner, E.; Maier, J. P. 68. The Electronic States of the Pentatetraene Radical Cation. *Helv. Chim. Acta* **1977**, *60*, 629.

[74] Grutzmacher, H. F.; Lohmann, J. Massenspektrometrie Instabiler Organischer Molekule. I. Ionisations-Potential und Bildungsenthalpie von Dehydrobenzol. *Ann. Chem.* **1967**, *705*, 81-90.

[75] Hemmersbach, P.; Klessinger, M.; Bruckmann, P. Electronic Structure of Exo-Dimethylenecycloalkanes. *J. Am. Chem. Soc.* **1978**, *100*, 6344-6347.

[76] Mamer, A.; Lossing, F. P.; Hedaya, E.; Kent, M. E. Pyrolysis of Bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic Anhydride. *Can. J. Chem.* **1970**, *48*, 3606-3608.

[77] Bally, T.; Hasselmann, D.; Loosen, K. 41. The Molecular Ion of 5-Methylene-1,3-cyclohexadiene: Electronic Absorption Spectrum and Revised Enthalpy of Formation. *Helv. Chim. Acta* **1985**, *68*, 345-354.

[78] Gleiter, R.; Krennrich, G.; Brinker, U. H. Electronic Structure of Spiropentane and Some Derivatives. *J. Org. Chem.* **1986**, *51*, 2899-2901.

[79] Abeywickrema, R. S.; Della, E. W.; Pigou, P. E.; Livett, M. K.; Peel, J. B. Orbital Interactions in Some Polycycloalkyl Halides: A Photoelectron Spectroscopic Study. *J. Am. Chem. Soc.* **1984**, *106*, 7321-7327.

[80] Dewar, M. J. S.; Fonken, G. J.; Jones, T. B.; Minter, D. E. Photoelectron Ppectra of Molecules. Part VII. Cyclopropylallenes. *J. Chem. Soc. Perkin Trans. 2* **1976**, 764-767.

[81] Koenig, T.; Imre, D.; Hoobler, J. A. He(I) Photoelectron Spectrum of Benzocyclobutadiene. *J. Am. Chem. Soc.* **1979**, *101*, 6446-6447.

[82] Brogli, F.; Heilbronner, E.; Hornung, V.; Kloster-Jensen, E. 230. Die Photoelektronen-Spektren Methyl-Substituierter Acetylene. *Helv. Chim. Acta* **1973**, *56*, 2171-2178.

[83] Haselbach, E.; Heilbronner, E.; Schroder, G. The Interaction of π-Orbitals in Barrelene. *Helv. Chim. Acta* **1971**, *54*, 153-162.

[84] Gassman, P. G.; Yamaguchi, R. Electrochemical Oxidation of Strained Hydrocarbons. *J. Am. Chem. Soc.* **1979**, *101*, 1308-1310.

[85] Hoffmann, R. W.; Schuttler, R.; Schafer, W.; Schweig, A. Methylen-Norbornadien, ein Bicycloheptafulven. *Angew. Chem.* **1972**, *84*, 533-534.

[86] Gleiter, R.; Bischof, P.; Christl, M. Electronic Structure of Octavalene. Photoelectron Spectroscopic Investigations. *J. Org. Chem.* **1986**, *51*, 2895-2898.

[87] Meier, H.; Konig, P.; Molz, T.; Gleiter, R.; Schafer, W. Untersuchungen zur Konformation und Elektronischen Struktur von Cyclooctadieninen. *Chem. Ber.* **1985**, *118*, 210-220.

[88] Bally, T.; Truttmann, L.; Wang, J. T.; Williams, F. Electronic Structure and Photochemical Interconversions of Dihydropentalene Radical Cations. *J. Am. Chem. Soc.* **1995**, *117*, 7923-7934.

[89] Bally, T.; Buser, U.; Haselbach, E. L. Tetrakis(methylidene)cyclobutane(`[4]radialene'): Electronic States of the Molecular Ion. *Helv. Chim. Acta* **1978**, *61*, 38-45.

[90] Gleiter, R.; Haider, R.; Bischof, P.; Zefirov, N. S.; Boganov, A. M. Electronic Structure of the Tricyclo[2.1.0.$0^{2,5}$]pentane System. Photoelectron Spectroscopic Investigations of 1,5-Dimethyl-3-exo-methylenetricyclo[2.1.0.$0^{2,5}$]pentane and 1,5-Dimethyltricyclo[2.l.0.$0^{2,5}$]pentan-3-one. *J. Org. Chem.* **1984**, *49*, 375-377.

[91] Clark, P. A.; Gleiter, R.; Heilbronner, E. Photoelectron Spectra of Planar Sulfur. *J. Heterocycl. Chem.* **1973**, *29*, 3085.

[92] Breitenstein, M.; Schulz, R.; Schweig, A. Theory and Applications of Photoelectron Spectroscopy. 96. Photoelectron Spectrum and Infrared Spectrum of Thermally Generated Transient Benzodithiete. *J. Org. Chem.* **1982**, *47*, 1979-1980.

[93] Bloch, M.; Brogli, F.; Heilbronner, E.; Jones, T. B.; Prinzbach, H.; Schweikert, O. 138. Photoelectron Spectra of Unsaturated Oxides. I. 1,4- Dioxin and Related Systems. *Helv. Chim. Acta* **1978**, *6*, 1388-1398.

[94] Gleiter, R.; Kobayashi, M.; Neunhoeffer, H.; Spanget-Larsen, J. Photoelectron Spectra of 1,2,4-Triazine and Some Methyl Derivatives. *Chem. Phys. Lett.* **1977**, *46*, 231-235.

[95] Bock, H.; Dammel, R. Cycloalkanimine 2H-Azirin, 1-Azetin, 1-Pyrrolin, 1-Piperidein, und 3,4,5,6-Tetrahydro-2H-azepin: Darstellung und Photoelektronen-Spektren. *Chem. Ber.* **1987**, *120*, 1971-1985.

[96] Dammel, R.; Bock, H.; Denis, J. M. The Photoelectron Spectrum of 1-Azetine. *Chem. Phys. Lett.* **1983**, *102*, 239-243.

[97] Stafast, H.; Bock, H. Photoelektronenspektren und Molekuleigenschaften, XXXIV. Cyanamid. *Chem. Ber.* **1974**, *107*, 1882.

[98] 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.

[99] Kiser, R. W.; Gallegos, E. J. A Technique for the Rapid Determination of Ionization and Appearance Potentials. *J. Phys. Chem.* **1962**, *66*, 947-948.

[100] Bowers, M. T. *Gas Phase Ion Chemistry*; Academic Press: New York, NY, USA, 1979.

[101] 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.

[102] Morishima, I.; Yoshikawa, K.; Hashimoto, M.; Bekki, K. Homoallylic Interaction Between the Nitrogen Lone Pair and the Nonadjacent π Bond in Cyclic and Bicyclic Amines. I. Photoelectron Spectroscopic Study. *J. Am. Chem. Soc.* **1975**, *97*, 4283-4288.

[103] Guimon, C.; Khayar, S.; Pfister-Guillouzo, G.; Claramunt, R. M.; Elguero, J. A Direct Photoelectron Spectroscopy Study of the 1-Azidopyridine Pyrolysis. *Spectrosc. Lett.* **1982**, *15*, 435-438.

[104] Plemenkov, V. V.; Redchenko, V. V.; Ermolaeva, L. V.; Bolesov, I. G.; Gritsenko, E. I. Photoelectron Spectra and Molecular Orbitals of 1-Methyl-1-cyancyclopropane and 3-Methyl-3-cycanocyclopropene. *J. Gen. Chem. USSR* **1986**, *56*, 184.