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AM1* parameters for bromine and iodine

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Abstract Our extension of the AM1 semiempirical molecular orbital technique, AM1*, has been parameterized for the elements Br and I. The basis sets for both halogens contain a set of d-orbitals as polarization functions. AM1* performs as well as other MNDO-like methods that use d-orbitals in the basis, and better than those that rely on an sp-basis. Thus, AM1* parameters are now available for H, C, N, O and F (which use the original AM1 parameters), Al, Si, P, S, Cl, Ti, Cu, Zn, Br, Zr, Mo and I.

Keywords AM1* · Bromine parameters · Iodine parameters · Semiempirical MO-theory

Introduction

AM1* [1–3] is an extension of AM1 molecular orbital theory, [4] that uses d-orbitals for the elements P, S, Cl, [1] Al, Si, Ti and Zr, [2] Cu and Zn [3] and a slight modification of Voityuk and Rösch's AM1(d) parameters for Mo. [5] Our original motivation in parameterizing AM1* was to retain the advantages of AM1 (good energies for hydrogen bonds, higher rotation barriers for π-systems than MNDO [6, 7] or PM3 [8–10]) for the

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elements H, C, N, O and F; to improve performance over AM1 for P-, S- and Cl-containing compounds; and eventually to produce a published parameterization for an MNDO-like method for the transition metals. We now report AM1* parameters for bromine and iodine. Parameters for these elements became necessary in order to be able to parameterize the transition metals adequately by including their bromides and iodides in the parameterization dataset. In contrast to our work on Al, Si, Ti and Zr [2] and on Cu and Zn, [3] the available experimental data for bromine and iodine compounds is sufficient in both quantity and quality that we can rely mostly on experimental sources and have resorted to only a few data obtained by higher-level calculations.

Theory

AM1* for the two new elements uses the same basic theory as outlined previously, [1, 2] with the exception that the core–core repulsion potential for the Br–H and I–H interactions used a distance-dependent term δ_{ij}, rather than the constant term used for core–core potentials for most other interactions in AM1*. [1] A distance-dependent δ_{ij} was also used for the Mo–H and interaction in AM1(d) [5] and for Ti–H, Cu–H, Zn–H, Zr–H and Mo–H in AM1*. [2, 3] The core–core terms for Br–H and I–H are thus:

$$E^{core}(i-j) = Z_i Z_j \rho_{ss}^0 \left[1 + r_{ij}\delta_{ij} \exp\left(-\alpha_{ij} r_{ij}\right) \right] \qquad (1)$$

where all terms have the same meaning as given in reference [1].

The parameterization techniques were those reported in references [1] and [2] and will not be described further here.

Parameterization data

The target values used for parameterization and their sources are defined in Table S1 of the electronic supplementary material (ESM). As we did for the Ti, Zr and Cu, Zn parameterizations [2, 3], we have used both reaction energies and heats of formation, and have also used a small series of model compounds whose heats of formation we derived from DFT or ab initio calculations. As before [1–3], we checked that experimental values for heats of formation were reasonable using DFT calculations.

Experimental parameterization data were taken largely from the NIST Webbook, [11] but also from the OpenMopac collection [12] and the other experimental sources given in the ESM.

DFT calculations used the Gaussian 03 suite of programs [13] with the LANL2DZ basis set and standard pseudopotentials [14–17] augmented by a set of polarization functions [18] (designated LANL2DZ+pol) and the B3LYP hybrid functional [19–21]. In some cases, coupled cluster calculations with single and double excitations and a perturbational corrections for triples [CCSD(T)] [22–25] with the 6-311+G(d) basis set [26–31] were used to check values for which DFT may be unreliable. We paid special attention to the heats of formation of titanium and zirconium halides, some of which appear to be significantly in error. The data and reactions used to derive the recommended heats of formation for chlorides, bromides and iodides of these two elements are defined in detail in the ESM, as are the other parameterization data and their sources.

Results

The optimized AM1* parameters are shown in Table 1. Geometries were optimized with the new AM1* parameterization and for AM1 and PM3 using VAMP 10.0, [32] while the PM5 calculations used LinMOPAC2.0 [33] and those with PM6 used MOPAC2007. [34] The three programs give essentially identical results for the Hamiltonians that are available in all three.

Bromine

Heats of formation

The calculated heats of formation for our training set of bromine compounds are shown in Table 2. We have compared our results with the available published methods and the unpublished PM5 method implemented in LinMopac. [33] As Stewart's PM6 parameters are now

Table 1 AM1* parameters for the elements Br and I

Parameter	Br	I
U_{ss} [eV]	−65.40253456	−60.75271210
U_{pp} [eV]	−54.55391930	−47.18041426
U_{dd} [eV]	−15.51056900	−9.49851860
ζ_s [bohr^{-1}]	2.5905411	4.0425168
ζ_p [bohr^{-1}]	2.3308566	2.8124603
ζ_d [bohr^{-1}]	1.3573612	1.6540802
β_s [eV]	−8.3149757	−6.5019618
β_p [eV]	−10.5070410	−7.9162569
β_d [eV]	−0.9625993	−3.4072650
g_{ss} [eV]	7.4008761	8.9163551
g_{pp} [eV]	9.2274222	3.6086821
g_{sp} [eV]	7.5365165	9.1817156
g_{p2} [eV]	7.9550041	5.7144226
h_{sp} [eV]	3.6616527	2.9958452
z_{sn} [bohr^{-1}]	0.4804244	0.1695950
z_{pn} [bohr^{-1}]	3.7665928	2.2521795
z_{dn} [bohr^{-1}]	4.8057603	4.1070512
ρ(core) [bohr^{-1}]	1.7542911	1.3865333
ΔH°_f(atom) [kcal mol^{-1}]	26.7400000	25.5160000
F^0_{sd} [eV]	4.6747381	5.7882291
G^2_{sd} [eV]	26.6113981	15.4899237
$\alpha(ij)$		
H	3.7096163	3.8684681
C	2.5775014	2.8992533
N	2.8846137	2.9170659
O	3.5223744	2.4445019
F	2.4787667	2.3108956
Al	2.5933836	3.2803001
Si	4.0281236	3.5099969
P	1.4090763	3.2419093
S	2.4234321	1.8500840
Cl	1.9658508	3.4260883
Ti	3.1288615	3.7234443
Cu	4.2315726	4.1756457
Zn	7.2212087	4.6581564
Br	3.1162216	2.1827496
Zr	3.6415408	3.3752957
Mo	3.4837054	3.7083736
I	2.1827496	3.6483792
$\delta(ij)$		
H	−7.1316792	−15.2888133
C	3.0538542	9.9695358
N	5.7893235	9.0153552
O	11.8870965	2.6996725
F	1.6319315	1.8755240
Al	4.9508713	84.6788616
Si	72.6409601	68.6752217
P	0.6387116	50.7461936
S	3.1922391	2.1902606
Cl	1.0877097	30.6262179
Ti	8.5729464	87.8970995
Cu	61.7791246	91.5204213
Zn	3.0808859	77.1375232
Br	13.8079448	2.4789698
Zr	42.0142732	47.7961015
Mo	60.0988582	98.1745836
I	2.4789698	−40.7622533

Table 2 Calculated AM1*, MNDO/d, MNDO, AM1, PM3, PM5 and PM6 heats of formation and errors compared with our target values for the bromine compounds used to parameterize AM1* (all values kcal mol^{-1}). Errors are classified by coloring the boxes in which they appear: *Green* indicates errors lower than 10 kcal mol^{-1}, *yellow* 10–20 kcal mol^{-1}, and *pink* those greater than 20 kcal mol^{-1}

Compound	Target ΔH°f	AM1* ΔH°f	Error	MNDO/d ΔH°f	Error	MNDO ΔH°f	Error	AM1 ΔH°f	Error	PM3 ΔH°f	Error	PM5 ΔH°f	Error	PM6 ΔH°f	Error
Br	26.7	26.7	0.0	26.7	0.0	26.7	0.0	26.7	0.0	26.7	0.0	26.7	0.0	26.7	0.0
Br⁻	-50.9	-50.9	0.0	-50.9	0.0	-37.5	13.4	-20.4	30.5	-56.2	-5.3	-53.5	-2.6	-55.1	-4.2
Br⁺	273.2	273.2	0.0	264.3	-8.9	301.8	28.7	284.7	11.6	284.6	11.4	279.3	6.1	286	12.8
Br₂	7.4	7.9	0.5	6.7	-0.7	-1.7	-9.1	-5.3	-12.7	4.9	-2.5	-5.6	-13.0	2.5	-4.9
BrH	-8.7	-8.8	-0.1	2.8	11.5	3.6	12.3	-10.5	-1.8	5.3	14.0	-7.8	0.9	-15.7	-7.0
CH₃Br	-8.5	-6.2	2.3	-8.0	0.5	-10.4	-1.9	-6.2	2.3	-2.0	6.5	-7.5	1.0	-5.7	2.8
CH₂Br₂	0.0	-0.4	-0.4	-0.3	-0.3	-5.1	-5.1	-1.0	-1.0	7.9	7.9	-0.5	-0.5	2.8	2.8
CHBr₃	5.7	6.6	0.9	10.2	4.5	3.1	-2.6	6.4	0.7	17.6	11.9	9.3	3.6	12.4	6.7
CBr₄	20.1	14.0	-6.1	23.3	3.2	13.8	-6.3	15.9	-4.2	32.9	12.8	21.0	0.9	23.1	3.0
C₂H₅Br	-14.9	-14.3	0.6	-15.3	-0.4	-17.0	-2.1	-13.1	1.8	-11.4	3.5	-14.5	0.4	-13.0	1.9
CH₂Br-CH₂Br	-9.8	-9.5	0.3	-9.6	-0.2	-13.4	-3.6	-7.9	1.9	-3.4	6.4	-12.9	-3.1	-7.5	2.3
CHBr=CH₂	18.9	21.9	3.0	16.2	-2.7	15.8	-3.1	18.0	-0.9	23.8	4.9	16.8	-2.1	17.3	-1.6
1-C₃H₇Br	-20.8	-21.0	-0.2	-19.7	1.1	-21.6	-0.8	-19.5	1.3	-16.4	4.4	-20.0	0.8	-18.2	2.6
2-C₃H₇Br	-23.8	-20.3	3.5	-19.7	4.1	-20.6	3.2	-19.7	4.1	-20.8	3.0	-21.9	1.9	-21.9	1.9
1,2-C₃H₆Br₂	-17.1	-15.4	1.7	-13.0	4.1	-16.3	0.8	-12.1	5.0	-12.5	4.6	-19.6	-2.5	-17.5	-0.4
1,3-C₃H₆Br₂	-17.0	-16.4	0.6	-13.8	3.2	-17.9	-0.9	-14.5	2.5	-9.2	7.8	-17.7	-0.7	-13.7	3.3
(CH₂Br)HC=CH₂	10.8	11.2	0.4	8.5	-2.3	7.0	-3.8	11.0	0.2	13.4	2.6	9.1	-1.7	11.2	0.4
CH₃HC=CHBr cis	10.5	9.9	-0.6	6.2	-4.3	5.6	-4.9	7.9	-2.6	13.6	3.1	8.1	-2.4	9.9	-0.6
CH₃HC=CHBr trans	9.8	11.2	1.4	6.8	-3.0	6.4	-3.4	8.4	-1.4	17.8	8.0	9.1	-0.7	11.2	1.4
1-C₄H₉Br	-25.6	-27.8	-2.2	-24.9	0.7	-26.7	-1.1	-26.8	-1.2	-22.1	3.5	-25.6	0.0	-23.1	2.5
2-C₄H₉Br	-28.8	-25.9	2.9	-23.2	5.6	-24.2	4.6	-23.7	5.1	-25.6	3.2	-25.4	3.4	-24.4	4.4
C(CH₃)₃Br	-31.6	-24.1	7.5	-20.4	11.2	-20.5	11.1	-20.6	11.0	-30.3	1.3	-29.5	2.1	-31.7	-0.1
1-C₅H₁₁Br	-30.8	-34.7	-3.9	-29.6	1.2	-31.4	-0.6	-33.6	-2.8	-27.5	3.3	-31.0	-0.3	-28.1	2.7
C₆H₅Br	25.2	30.8	5.6	23.2	-2.0	23.9	-1.3	26.8	1.6	31.0	5.8	25.6	0.4	25.7	0.5
BrCN	44.4	47.8	3.4	40.2	-4.2	40.0	-4.4	32.5	-11.9	53.6	9.2	38.8	-5.6	35.1	-9.3
BrNO	19.6	19.6	0.0	8.0	-11.6	1.9	-17.7	21.3	1.7	6.6	-13.0	13.5	-6.1	-0.1	-19.7
BrO	30.1	30.1	0.0	29.9	-0.2	35.3	5.2	35.7	5.6	20.8	-9.3	25.9	-4.2	36.5	6.4
BrOH	-20.0	-30.9	-10.9	-24.0	-4.0	-22.7	-2.7	-24.7	-4.7	-33.9	-13.9	-19.6	0.4	-21.6	-1.6
O=CBr₂	-27.1	-25.8	1.3	-29.0	-1.9	-31.6	-4.5	-17.8	9.3	-25.3	1.8	-26.0	1.1	-25.7	1.4
CH₃COBr	-45.5	-40.4	5.1	-42.7	2.8	-43.2	2.3	-34.3	11.2	-43.5	2.0	-43.4	2.1	-44.6	0.9
CH₃COCH₂Br	-43.3	-42.8	0.5	-42.9	0.4	-43.2	0.1	-41.5	1.8	-42.9	0.4	-46.6	-3.3	-46.9	-3.6
C₆H₅-COBr	-11.6	-6.2	5.4	-7.5	4.1	-7.7	3.9	0.8	12.4	-7.7	3.9	-10.5	1.1	-7.6	4.0
p-Br-C₆H₄-COOH	-69.4	-57.9	11.5	-64.9	4.5	-64.3	5.1	-62.3	7.1	-57.9	11.5	-64.3	5.1	-62.1	7.3
BrF	-14.0	-27.4	-13.4	-26.0	-12.0	-5.8	8.2	-7.2	6.8	-21.2	-7.2	-10.6	3.4	-25.9	-11.9
BrF₂	-27.1	-34.8	-7.7	-28.7	-1.6	22.0	49.1	14.1	41.2	-11.7	15.4	-13.6	13.5	-33.9	-6.8
BrF₃	-61.1	-59.1	2.0	-59.6	1.5	22.9	84.0	24.9	86.0	-47.1	14.0	-51.3	9.8	-68.7	-7.6
BrF₅	-102.5	-102.5	0.0	-103.6	-1.1	107.7	210.2	83.4	185.9	-74.8	27.7	-108.9	-6.4	-81.3	21.2
CBrF₃	-155.1	-155.8	-0.7	-154.0	1.1	146.6	301.7	-144.6	10.5	-157.8	-2.7	-151.5	3.6	-150.2	4.9
CBr₂F₂	-91.0	-92.7	-1.7	-94.8	-3.8	-86.1	4.9	-74.1	16.9	-94.1	-3.1	-86.2	4.8	-84.3	6.7
CHBrF₂	-101.6	-105.9	-4.3	-105.1	-3.5	-101.1	0.5	-96.8	4.8	-99.4	2.2	-100.1	1.5	-95.8	5.8
CBrF₂-CBrF₂	-189.0	-184.2	4.8	-181.9	7.1	172.2	361.2	-165.3	23.7	-193.4	-4.4	-182.4	6.8	-184.5	4.5
CF₂Br-CH₂Br	-103.0	-94.2	8.8	-96.0	7.0	-92.9	10.1	-88.6	14.4	-100.3	2.7	-90.9	12.1	-90.2	12.8
CH₂F-CH₂Br	-60.0	-60.6	-0.6	-58.7	1.3	-60.8	-0.8	-60.7	-0.7	-51.2	8.8	-59.6	0.4	-56.8	3.2
C₆F₅Br	-191.3	-179.0	12.3	-193.9	-2.5	-192.0	-0.6	-179.7	11.6	-176.0	15.3	-178.8	12.5	-189.4	1.9
BrFO₃	32.8	101.2	68.4	31.5	-1.3	263.6	230.8	202.7	169.9	140.1	107.3	48.0	15.2	91.5	58.7
BrCl	3.5	3.5	0.0	0.0	-3.5	-9.5	-13.0	-10.6	-14.1	-3.2	-6.7	-8.3	-11.8	4.8	1.3
CBr₂Cl₂	2.0	0.4	-1.7	-3.5	-5.5	-5.1	-7.1	-2.7	-4.7	-1.6	-3.6	-0.3	-2.3	11.0	9.0
CBrCl₃	-10.0	-17.9	-7.9	-17.8	-7.8	-15.1	-5.1	-14.7	-4.7	-14.1	-4.1	-12.0	-2.0	-3.5	6.5
CHBr₂Cl	2.0	1.8	-0.2	-2.2	-4.2	-7.2	-9.2	-3.7	-5.7	3.2	1.2	-1.2	-3.2	6.9	4.9
CHBrCl₂	-12.0	-10.8	1.2	-15.3	-3.3	-17.9	-5.9	-15.5	-3.5	-9.0	3.0	-12.4	-0.4	-4.2	7.8
CH₃-CHClBr	-20.0	-15.9	4.1	-18.4	1.6	-21.2	-1.2	-17.5	2.5	-15.9	4.1	-19.5	0.5	-16.5	3.5

Table 2 (continued)

Compound	Target ΔH°f	AM1* ΔH°f	Error	MNDO/d ΔH°f	Error	MNDO ΔH°f	Error	AM1 ΔH°f	Error	PM3 ΔH°f	Error	PM5 ΔH°f	Error	PM6 ΔH°f	Error
CH₂Cl-CH₂Br	-19.4	-18.7	0.7	-19.3	0.1	-23.7	-4.3	-20.2	-0.8	-12.9	6.5	-22.8	-3.4	-16.4	3.0
CHBrCl-CHBrCl	-8.8	-8.6	0.2	-9.7	-0.9	-15.6	-6.8	-12.8	-4.0	-8.9	-0.1	-15.5	-6.7	-5.1	3.7
CBrClF₂	-105.0	-131.0	-26.0	-106.2	-1.2	-98.0	7.0	-90.0	15.0	-104.8	0.2	-99.6	5.4	-100.6	4.4
AlBr	3.8	4.4	0.6	4.5	0.7	0.7	-3.1	-0.3	-4.1	7.8	4.0	4.0	0.2	-3.7	-7.5
AlBr₃	-98.1	-88.9	9.2	-104.3	-6.2	-60.3	37.8	-96.4	1.7	-85.8	12.3	-94.7	3.4	-100.3	-2.2
Al₂Br₆	-224.0	-224.0	0.0	-222.9	1.1	-132.6	91.4	-248.9	-24.9	-224.9	-0.9	-224.4	-0.4	-222.5	1.5
BrSi	50.0	37.7	-12.3	50.1	0.1	79.3	29.3	46.1	-3.9	75.9	25.9	56.2	6.2	54.4	4.4
Br₂Si	-12.5	-15.0	-2.5	-3.7	8.8	11.2	23.7	-18.9	-6.4	-27.4	-14.9	-19.3	-6.8	-8.5	4.0
Br₃Si	-48.2	-61.2	-13.0	-34.7	13.5	-16.3	31.9	-66.8	-18.5	-61.6	-13.4	-54.3	-6.1	-48.1	0.1
Br₄Si	-99.3	-99.3	0.0	-73.1	26.2	-50.4	48.9	-94.5	4.8	-107.9	-8.6	-98.3	1.0	-98.9	0.4
BrH₃Si	-15.3	-15.0	0.3	-11.1	4.2	-18.0	-2.7	-21.1	-5.8	-16.0	-0.7	-18.4	-3.1	-17.7	-2.4
Br₂H₂Si	-43.2	-41.4	1.8	-31.6	11.6	-32.0	11.2	-45.8	-2.6	-47.2	-4.0	-45.9	-2.7	-44.5	-1.3
Br₃HSi	-72.5	-70.0	2.5	-52.2	20.3	-42.4	30.1	-70.2	2.3	-79.5	-7.0	-72.3	0.2	-72.2	0.3
BrP	38.9	39.9	1.0	65.0	26.1	38.1	-0.8	32.7	-6.2	40.3	1.4	80.8	41.9	36.1	-2.8
Br₃P	-33.2	-20.2	13.1	-25.2	8.0	-38.1	-4.9	-23.3	9.9	-28.2	5.0	-53.9	-20.7	-47.0	-13.8
Br₃P⁻	-70.0	-87.0	-17.0	-85.7	-15.7	-114.4	-44.4	-98.1	-28.1	-107.1	-37.1	-130.4	-60.4	-92.7	-22.7
Br₄P⁻	-99.7	-106.2	-6.5	-107.9	-8.2	-147.4	-47.7	-111.3	-11.6	-138.6	-38.9	-170.9	-71.2	-118.2	-18.5
Br₃PO	-97.0	-57.4	39.6	-82.5	14.5	-28.6	68.4	-29.0	68.0	-79.8	17.2	-91.2	5.8	-93.9	3.1
Br₂S	-3.0	-1.0	2.0	11.1	14.1	-0.2	2.8	-6.8	-3.8	24.4	27.4	-3.1	-0.1	-3.0	0.0
Br₂S₂	7.4	-8.1	-15.5	10.7	3.3	1.5	-5.9	-4.4	-11.8	21.8	14.4	-5.1	-12.5	-1.2	-8.6
SO₂Br⁻	-141.1	-141.1	0.0	-127.8	13.3	-74.2	66.9	-122.0	19.2	-137.5	3.6	-252.3	-111.2	-131.2	9.9
ZnBr	29.0	30.9	1.9	23.9	-5.1	10.6	-18.4	-12.8	-41.8	6.8	-22.3	-1.0	-30.0	-17.3	-46.3
ZnBr₂	-44.4	5.0	49.4	-35.7	8.7	2.7	47.1	-63.1	-18.7	-21.2	23.2	-35.1	9.3	-32.5	11.9
		AM1*		**MNDO/d**		**MNDO**		**AM1**		**PM3**		**PM5**		**PM6**	
Most positive error		68.4		26.2		361.2		185.9		107.3		41.9		58.7	
Most negative error		-26.0		-15.7		-47.7		-41.8		-38.9		-111.2		-46.3	
MSE		1.7		1.7		21.4		7.5		3.8		-3.0		0.9	
MUE		5.9		5.3		28.5		14.8		9.8		8.1		6.4	
RMSD		12.5		7.7		70.0		34.1		17.1		18.8		11.2	

Compounds Containing Ti, Cu, Zr and Mo.

Compound	Target ΔH°f	AM1* ΔH°f	Error									PM5 ΔH°f	Error	PM6 ΔH°f	Error
TiBr	51.0	1.5	-49.5									-1.0	-52.0	12.7	-38.3
TiBr₂	-30.0	-66.9	-36.9									-53.6	-23.6	-34.9	-4.9
TiBr₃	-90.0	-90.0	0.0									-95.7	-5.7	-88.8	1.2
TiBr₄	-132.0	-99.3	32.7									-130.5	1.5	-130.1	1.9
CuBr	41.3	34.3	-7.0									32.5	-8.8	16.0	-8.8
CuBr₂	22.4	34.1	11.7									-10.5	-32.9	29.1	6.7
CuOBr	15.7	22.5	6.8									47.8	32.1	66.0	50.3
ZrBr	80.0	32.3	-47.7									55.8	-24.2	64.3	-15.7
ZrBr₂	-7.5	-14.5	-7.0									-38.4	-30.9	-27.4	-19.9
ZrBr₃	-80.0	-79.4	0.6									-102.8	-22.8	-97.8	-17.8
ZrBr₄	-142.0	-113.8	28.2									-171.7	-29.7	-132.4	9.6
MoBr	109.3	139.1	29.8									185.2	75.9	126.3	17.0
MoBr₂	40.0	37.5	-2.5									109.0	69.0	68.4	28.4
MoBr₃	-2.0	0.5	2.5									-10.6	-8.6	15.9	17.9
MoBr₄	-40.9	-42.4	-1.5									-37.2	3.7	-44.8	-3.9
		AM1*										**PM5**		**PM6**	
Most positive error		32.7										75.9		50.3	
Most negative error		-49.5										-52.0		-38.3	
MSE		-2.7										-3.8		1.6	
MUE		17.6										28.1		16.1	
RMSD		24.7										35.6		21.0	

Table 3 Calculated AM1*, MNDO/d, MNDO, AM1, PM3, PM5 and PM6 Koopmans' theorem ionization potentials and dipole moments for bromine-containing compounds. The errors are color coded as follows: *green* up to 0.5 eV or 0.5 Debye; *yellow* between 0.5 and 1.0; *pink* larger than 1.0

Compound	Target	AM1*	Error	MNDO/d	Error	MNDO	Error	AM1	Error	PM3	Error	PM5	Error	PM6	Error
Koopmans' Theorem Ionization Potentials for Bromine Compounds (eV)															
Br_2	10.56	10.91	0.35	10.33	-0.23	11.66	1.10	10.94	0.38	11.24	0.68	10.80	0.24	10.71	0.15
BrH	11.71	10.89	-0.82	10.58	-1.13	12.10	0.39	11.46	-0.25	12.13	0.42	11.31	-0.40	11.14	-0.57
CH_3Br	10.54	10.43	-0.11	10.30	-0.24	11.56	1.02	10.80	0.26	11.01	0.47	10.51	-0.03	10.62	0.08
CH_2Br_2	10.61	10.77	0.16	10.48	-0.13	11.70	1.09	10.96	0.35	10.59	-0.02	10.59	-0.02	10.60	-0.01
$CHBr_3$	10.47	11.10	0.63	10.61	0.14	11.87	1.40	11.07	0.60	10.84	0.37	10.67	0.20	10.75	0.28
CBr_4	10.40	11.38	0.98	10.74	0.34	12.03	1.63	11.22	0.82	11.22	0.82	10.72	0.32	10.93	0.53
C_2H_5Br	10.28	10.33	0.05	10.24	-0.04	11.48	1.20	10.69	0.41	10.91	0.63	10.40	0.12	10.47	0.19
$CHBr=CH_2$	9.80	10.10	0.30	9.69	-0.11	10.25	0.45	10.15	0.35	10.44	0.64	10.06	0.26	10.22	0.42
$1\text{-}C_3H_7Br$	10.18	10.33	0.15	10.23	0.05	11.46	1.28	10.65	0.47	10.85	0.67	10.40	0.22	10.48	0.30
$1\text{-}C_4H_9Br$	10.15	10.33	0.18	10.23	0.08	11.47	1.32	10.69	0.54	10.92	0.77	10.40	0.25	10.48	0.33
C_6H_5Br	9.25	9.68	0.43	9.28	0.03	9.55	0.30	9.60	0.35	9.81	0.56	9.45	0.20	9.65	0.40
$BrCN$	11.88	11.40	-0.48	10.85	-1.03	12.40	0.52	11.92	0.04	11.72	-0.16	11.41	-0.47	11.74	-0.14
$O=CBr_2$	11.00	11.18	0.18	10.88	-0.12	11.89	0.89	11.31	0.31	10.95	-0.05	11.21	0.21	10.92	-0.08
CH_3COBr	10.55	10.72	0.17	10.66	0.11	11.43	0.88	11.18	0.63	11.20	0.65	11.05	0.50	10.88	0.33
BrF	11.87	10.84	-1.03	10.80	-1.07	12.65	0.78	11.77	-0.10	11.64	-0.23	11.56	-0.31	11.53	-0.34
BrF_3	12.38	10.83	-1.55	11.45	-0.93	13.89	1.51	12.51	0.13	12.46	0.08	12.37	-0.01	12.10	-0.28
$CBrF_3$	12.10	11.52	-0.58	11.56	-0.54	13.25	1.15	12.33	0.23	12.23	0.13	12.26	0.16	12.00	-0.10
$CBrF_2\text{-}CBrF_2$	12.76	11.18	-1.58	11.42	-1.34	12.77	0.01	11.49	-1.27	11.03	-1.73	11.71	-1.05	11.55	-1.21
$AlBr_3$	10.91	11.59	0.68	10.85	-0.06	12.04	1.13	11.50	0.59	14.31	3.40	11.11	0.20	10.92	0.01
Br_2H_2Si	10.92	10.92	0.00	11.21	0.29	11.75	0.83	11.11	0.19	11.45	0.53	10.50	-0.42	10.65	-0.28
Br_3PO	11.08	11.92	0.84	11.57	0.49	12.18	1.10	12.09	1.01	12.70	1.62	11.91	0.83	11.46	0.38
$BrCl$	11.10	10.76	-0.34	10.51	-0.59	12.01	0.91	11.22	0.12	10.92	-0.18	10.87	-0.23	10.82	-0.28
$ZnBr_2$	11.06	10.90	-0.16	10.48	-0.58	11.76	0.70	11.36	0.30	12.62	1.56	11.17	0.11	11.07	0.01
MSE			-0.07		-0.29		0.94		0.28		0.51		0.04		0.01
MUE			0.51		0.42		0.94		0.42		0.71		0.29		0.29
Dipole Moments for Bromine Containing Compounds (Debye)															
BrH	0.83	0.95	0.12	1.16	0.33	1.07	0.24	1.38	0.55	1.27	0.44	1.32	0.49	1.16	0.33
CH_3Br	1.82	1.61	-0.21	1.87	0.05	1.56	-0.26	1.47	-0.35	1.55	-0.27	1.80	-0.02	1.58	-0.24
CH_2Br_2	1.43	1.34	-0.09	1.60	0.17	1.37	-0.06	1.32	-0.11	1.45	0.02	1.48	0.05	1.42	-0.01
$CHBr_3$	0.99	0.89	-0.10	1.06	0.07	0.91	-0.08	0.91	-0.08	0.96	-0.03	0.94	-0.05	1.00	0.01
C_2H_5Br	2.03	1.94	-0.09	1.98	-0.05	1.66	-0.37	1.66	-0.37	1.85	-0.18	2.20	0.17	2.09	0.06
$CHBr=CH_2$	1.42	1.67	0.25	1.62	0.20	1.31	-0.11	1.30	-0.12	1.33	-0.09	1.58	0.16	1.51	0.09
$1\text{-}C_3H_7Br$	2.18	1.99	-0.19	1.97	-0.21	1.64	-0.54	1.65	-0.53	1.80	-0.38	2.19	0.01	2.14	-0.04
$2\text{-}C_3H_7Br$	2.21	2.18	-0.03	2.07	-0.14	1.72	-0.49	1.79	-0.42	2.05	-0.16	2.49	0.28	2.62	0.41
$1\text{-}C_4H_9Br$	2.10	2.02	-0.08	2.06	-0.04	1.73	-0.37	1.72	-0.38	1.82	-0.28	2.21	0.11	2.14	0.04
$1\text{-}C_5H_{11}Br$	2.13	2.05	-0.08	2.08	-0.05	1.75	-0.38	1.74	-0.39	1.84	-0.29	2.24	0.11	2.20	0.07
C_6H_5Br	1.70	1.87	0.17	1.70	0.00	1.80	0.10	1.41	-0.29	1.45	-0.25	1.50	-0.20	1.78	0.08
$BrNO$	1.80	2.43	0.63	1.19	-0.61	1.19	-0.61	0.95	-0.85	0.87	-0.93	1.26	-0.54	2.39	0.59
BrO	1.55	1.22	-0.33	1.52	-0.03	1.19	-0.36	2.36	0.81	2.08	0.53	2.78	1.23	1.95	0.40
CH_3COBr	2.43	3.00	0.57	2.57	0.14	2.45	0.02	2.59	0.16	2.95	0.52	3.34	0.91	3.38	0.95
BrF	1.42	1.35	-0.07	1.50	0.08	2.10	0.68	1.46	0.04	2.25	0.83	2.54	1.12	0.80	-0.62
BrF_3	1.19	2.32	1.13	2.78	1.59	0.00	-1.19	2.53	1.34	0.00	-1.19	0.00	-1.19	0.02	-1.17
$BrHCF_2$	1.31	1.71	0.40	1.85	0.54	1.74	0.43	1.55	0.24	1.57	0.26	2.19	0.88	1.56	0.25
CBr_2F_2	0.66	0.45	-0.21	0.77	0.11	0.83	0.17	0.60	-0.06	0.54	-0.12	1.42	0.76	0.63	-0.03
$CBrF_3$	0.63	0.63	0.00	0.96	0.33	1.18	0.55	1.02	0.39	0.91	0.28	1.50	0.87	0.99	0.36
BrH_3Si	1.32	3.62	2.30	1.56	0.24	3.45	2.13	1.81	0.49	2.26	0.94	2.62	1.30	1.62	0.30
$BrCl$	0.52	0.86	0.34	0.43	-0.09	0.75	0.23	0.45	-0.07	0.06	-0.46	0.89	0.37	0.60	0.08
MSE			0.21		0.13		-0.01		0.00		-0.04		0.32		0.09
MUE			0.35		0.24		0.45		0.38		0.40		0.52		0.29

Table 4 Calculated AM1*, MNDO/d, MNDO, AM1, PM3, PM5 and PM6 bond lengths and angles for bromine-containing compounds. The errors are color coded as follows: *green* up to 0.05 Å or 0.5°; *yellow* between 0.05 and 0.1 Å or 0.5–1.0°; *pink* greater than 0.1 Å or 1°

Compound	Variable	Target	AM1*	Error	MNDO/d	Error	MNDO	Error	AM1	Error	PM3	Error	PM5	Error	PM6	Error
BrH	Br-H	1.42	1.42	0.00	1.44	0.03	1.44	0.02	1.42	0.01	1.47	0.05	1.38	-0.04	1.45	0.03
CH₃Br	Br-C	1.93	1.91	-0.02	1.92	-0.02	1.88	-0.06	1.90	-0.03	1.95	0.02	2.50	0.56	1.95	0.01
CH₂Br₂	Br-C	1.93	1.90	-0.03	1.92	-0.01	1.87	-0.06	1.90	-0.02	1.91	-0.01	1.92	-0.01	1.94	0.01
	Br-C-Br	112.9	109.4	-3.5	113.1	0.2	111.7	-1.2	113.7	0.8	94.4	-18.5	109	-3.9	111.5	-
	Br-C-H	109.0	108.0	-1.0	108.4	-0.6	108.6	-0.4	108.2	-0.8	112.5	3.5	108.6	-0.4	108.8	-
CHBr₃	Br-C	1.92	1.90	-0.03	1.92	0.00	1.86	-0.06	1.91	-0.02	1.87	-0.05	1.91	-0.02	1.93	0.01
	Br-C-Br	111.7	109.7	-2.0	111.4	-0.3	110.7	-1.0	111.7	0.0	98.4	-13.3	109.3	-2.4	110.7	-
CBr₄	Br-C	1.93	1.90	-0.03	1.93	0.00	1.86	-0.07	1.92	-0.01	1.84	-0.09	1.90	-0.03	1.94	0.01
CBrCl₃	Br-C	1.93	1.97	0.04	1.95	0.02	1.87	-0.05	1.96	0.03	1.91	-0.01	1.93	0.00	1.96	0.
	Br-C-Cl	109.2	110.7	1.5	110.3	1.1	109.6	0.4	109.3	0.1	105.3	-3.9	108.6	-0.6	110.6	
CBrF₃	Br-C	1.92	1.95	0.03	1.95	0.03	1.94	0.01	2.04	0.12	1.96	0.04	1.99	0.06	1.98	0.06
C₂H₅Br	Br-C	1.95	1.93	-0.02	1.93	-0.02	1.89	-0.06	1.93	-0.02	1.96	0.01	1.96	0.01	1.98	0.03
	Br-C-C	111.0	110.6	-0.4	112.5	1.5	112.7	1.7	113.5	2.5	104.4	-6.6	108	-3.0	111.2	
CH₂Br-CH₂Br	Br-C	1.95	1.93	-0.02	1.93	-0.02	1.89	-0.06	1.93	-0.02	1.96	0.01	1.96	0.01	1.97	0.02
	Br-C-C	109.5	109.0	-0.5	111.0	1.5	111.2	1.7	112.0	2.5	103.9	-5.6	105.8	-3.7	109.4	-
CH₂=CHBr	Br-C	1.88	1.88	0.00	1.87	-0.02	1.83	-0.05	1.86	-0.02	1.90	0.01	1.90	0.02	1.91	0.03
	Br-C=C	122.8	121.4	-1.4	123.3	0.5	123.8	1.0	125.1	2.3	116.2	-6.6	119.7	-3.1	122.4	-
1-C₃H₇Br	Br-C	1.97	1.93	-0.04	1.93	-0.04	1.89	-0.08	1.93	-0.04	1.96	-0.01	1.96	0.01	1.97	0.00
	Br-C-C	111.0	110.4	-0.6	113.4	2.4	113.8	2.8	114.5	3.5	105.2	-5.8	107.7	-3.3	110.8	-
2-C₃H₇Br	Br-C	1.96	1.95	-0.01	1.94	-0.02	1.90	-0.05	1.95	0.00	1.96	0.01	1.98	0.02	2.01	0.06
	Br-C-C	111.0	108.3	-2.7	109.5	-1.5	109.4	-1.6	111.0	0.0	103.9	-7.1	106.3	-4.7	108.5	-
1,3-C₃H₆Br₂	Br-C	1.96	1.93	-0.03	1.93	-0.03	1.89	-0.07	1.93	-0.03	1.96	0.00	1.95	-0.01	1.97	0.01
	Br-C-C	112.0	110.0	-2.0	113.3	1.3	113.6	1.6	114.3	2.3	105.1	-6.9	107.4	-4.6	110.5	-
(CH₃)HC=CHBr trans	Br-C	1.88	1.93	0.04	1.86	-0.02	1.83	-0.05	1.86	-0.03	1.89	0.01	1.96	0.08	1.97	0.08
	Br-C=C	122.1	114.3	-7.8	126.0	3.9	126.7	4.6	127.3	5.2	119.7	-2.4	112.6	-9.5	115.3	-
(CH₂Br)HC=CH₂	Br-C	1.96	1.93	-0.03	1.93	-0.03	1.90	-0.07	1.93	-0.03	1.96	0.00	1.96	0.00	1.97	0.01
	Br-C-C	111.5	114.2	2.7	110.5	-1.0	111.0	-0.5	112.0	0.5	104.0	-7.5	112.7	1.2	115.2	
1-C₄H₉Br	Br-C	1.95	1.93	-0.02	1.93	-0.02	1.89	-0.06	1.93	-0.02	1.96	0.01	1.96	0.01	1.97	0.02
	Br-C-C	111.0	110.3	-0.7	111.8	0.8	112.0	1.0	113.3	2.3	104.2	-6.8	107.5	-3.5	110.8	-
(CH₃)₃CBr	Br-C	1.98	1.97	-0.01	1.96	-0.02	1.92	-0.05	1.98	0.00	1.96	-0.01	2.00	0.02	2.05	0.07
C₆H₅Br	Br-C	1.85	1.88	0.03	1.86	0.01	1.83	-0.02	1.87	0.02	1.87	0.02	1.88	0.03	1.92	0.06
O=CBr₂	Br-C	1.92	1.89	-0.03	1.90	-0.02	1.85	-0.06	1.92	0.00	1.90	-0.02	1.90	-0.02	1.94	0.02
	Br-C-Br	112.3	112.7	0.4	115.6	3.3	111.2	-1.1	110.6	-1.7	97.4	-14.9	125.9	13.6	109.9	-
CH₃COBr	Br-C	1.97	1.93	-0.04	1.92	-0.05	1.89	-0.09	1.95	-0.03	1.97	-0.01	1.96	-0.02	2.00	0.03
	Br-C=O	121.9	116.3	-5.6	118.2	-3.7	119.8	-2.1	122.5	0.6	119.3	-2.6	119.6	-2.3	120.6	-
	Br-C-C	111.0	113.1	2.1	114.3	3.3	112.9	1.9	113.3	2.3	106.3	-4.7	108.1	-2.9	110.8	-
BrCN	Br-C	1.79	1.81	0.02	1.78	-0.01	1.74	-0.05	1.76	-0.03	1.80	0.01	1.78	-0.01	1.77	-0.02
BrNO	Br-N	2.14	2.07	-0.07	1.91	-0.23	1.87	-0.27	1.92	-0.22	1.89	-0.25	1.92	-0.22	2.05	-0.09
	Br-N=O	114.5	113.2	-1.3	117.5	3.0	118.9	4.4	122.5	8.0	120.8	6.3	120.3	5.8	119.9	
BrO	Br-O	1.72	1.85	0.13	1.69	-0.02	1.70	-0.02	1.79	0.08	1.76	0.04	1.71	-0.01	1.79	0.07
BrF	Br-F	1.76	1.72	-0.03	1.76	0.00	1.73	-0.03	1.78	0.02	1.77	0.02	1.76	0.00	1.77	0.01
BrF₃	Br-Fₐₓ	1.73	1.73	0.00	1.77	0.04	1.76	0.03	1.81	0.08	1.79	0.06	1.74	0.01	1.77	0.04
	Br-F_eq	1.81	1.76	-0.05	1.82	0.02	1.76	-0.05	1.82	0.01	1.79	-0.02	1.74	-0.07	1.77	-0.04
	Fₐₓ-Br-F_eq	85.0	83.1	-2.0	83.3	-1.7	120.0	35.0	81.4	-3.6	120.0	35.0	120	35.0	120.6	35.6
BrF₅	Br-Fₐₓ	1.70	1.72	0.02	1.78	0.09	1.77	0.07	1.82	0.13	1.76	0.06	1.69	-0.01	1.78	0.08
	Br-F_eq	1.77	1.74	-0.03	1.81	0.04	1.77	0.00	1.80	0.03	1.77	0.01	1.70	-0.06	1.76	-0.01
	Fₐₓ-Br-F_eq	84.8	84.8	0.00	83.6	-1.2	104.7	19.9	85.2	0.4	103.6	18.8	103	18.2	88.7	
BrFO₃	Br-F	1.71	1.71	0.00	1.77	0.06	1.78	0.08	1.81	0.10	1.78	0.08	1.71	0.00	1.70	-0.01
	Br=O	1.58	1.83	0.25	1.62	0.04	1.79	0.21	1.87	0.29	1.78	0.19	1.72	0.14	1.49	-0.09
	F-Br=O	103.3	98.9	-4.4	102.5	-0.8	105.7	2.4	98.5	-4.8	108.2	4.9	102.1	-1.2	100.1	-
	O=Br=O	114.9	107.3	-7.6	115.5	0.6	113.0	-1.9	117.8	2.9	110.7	-4.2	114.1	-0.8	105.5	-
BrCl	Br-Cl	2.14	1.97	-0.17	2.11	-0.02	2.08	-0.06	2.06	-0.07	2.18	0.04	2.11	-0.02	2.18	0.04
Br₂	Br-Br	2.28	2.28	0.00	2.27	-0.01	2.17	-0.11	2.18	-0.10	2.44	0.16	2.24	-0.04	2.33	0.05
AlBr	Br-Al	2.30	2.08	-0.22	2.27	-0.03	2.20	-0.09	2.26	-0.03	2.29	0.00	2.22	-0.07	2.29	0.00

Table 4 (continued)

Compound	Variable	Target	AM1*	Error	MNDO/d	Error	MNDO	Error	AM1	Error	PM3	Error	PM5	Error	PM6	Error
Al₂Br₆	Br-Al	2.22	2.08	-0.14	2.23	0.01	2.18	-0.04	2.27	0.04	1.84	-0.38	2.18	-0.04	2.23	0.01
	Br-Al(2)	2.38	2.24	-0.14	2.49	0.11	2.39	0.01	2.40	0.02	2.46	0.08	2.39	0.00	2.44	0.06
	Br-Al-Br	118.0	126.0	8.0	123.1	5.1	122.1	4.1	119.4	1.4	104.2	-13.8	122.1	4.1	124.2	
BrSi	Br-Si	2.25	2.25	0.00	2.21	-0.04	2.20	-0.06	2.17	-0.08	1.85	-0.40	2.02	-0.23	2.26	0.01
Br₂Si	Br-Si	2.24	2.24	0.00	2.24	-0.01	2.21	-0.03	2.20	-0.05	1.86	-0.39	2.23	-0.01	2.10	-0.14
Br₄Si	Br-Si	2.18	2.26	0.07	2.22	0.04	2.19	0.01	2.24	0.06	1.80	-0.39	2.22	0.04	2.17	-0.01
BrH₃Si	Br-Si	2.21	2.30	0.09	2.24	0.03	2.23	0.02	2.24	0.03	1.90	-0.31	2.27	0.06	2.23	0.02
	Br-Si-H	108.2	104.9	-3.3	108.3	0.1	106.9	-1.3	110.4	2.2	108.3	0.1	106.1	-2.1	108.9	
Br₃P	Br-P	2.22	1.96	-0.26	2.18	-0.04	2.09	-0.13	2.10	-0.12	2.09	-0.13	2.22	0.00	2.19	-0.03
	Br-P-Br	101.0	107.7	6.7	105.3	4.3	105.7	4.7	106.8	5.8	87.1	-13.9	104.6	3.6	104.6	
Br₃PO	Br-P	2.17	1.99	-0.18	2.21	0.03	2.13	-0.05	2.16	-0.01	2.05	-0.12	2.21	0.04	2.18	0.01
	O=P	1.46	1.50	0.04	1.49	0.03	1.48	0.02	1.48	0.02	1.41	-0.05	1.36	-0.10	1.49	0.03
	O=P-Br	114.2	113.1	-1.1	114.8	0.6	113.8	-0.4	115.2	1.0	125.5	11.3	115.2	1.0	114.5	
Br₂S₂	Br-S	2.24	2.22	-0.02	2.17	-0.07	2.07	-0.17	2.12	-0.13	2.25	0.01	2.17	-0.07	2.11	-0.13
Br₂SO	Br-S	2.23	2.24	0.00	2.24	0.00	2.14	-0.09	2.21	-0.03	2.33	0.10	2.21	-0.03	2.17	-0.06
	S=O	1.45	1.53	0.08	1.50	0.05	1.47	0.02	1.46	0.01	1.45	0.00	1.43	-0.02	1.44	-0.01
	O=S-Br	107.6	108.9	1.3	108.5	0.9	108.0	0.4	111.0	3.4	103.4	-4.2	109.9	2.3	114.0	
	Br-S-Br	98.2	97.2	-1.0	101.2	3.0	103.6	5.4	103.8	5.6	99.7	1.5	107.5	9.3	100.2	
ZnBr₂	Br-Zn	2.20	2.09	-0.11	2.17	-0.04	2.24	0.03	2.11	-0.09	2.10	-0.11	2.24	0.04	2.21	0.01
			AM1*		**MNDO/d**		**MNDO**		**AM1**		**PM3**		**PM5**		**PM6**	
MSE bond length			-0.02		0.00		-0.04		0.00		-0.04		0.00		0.01	
MUE bond length			0.06		0.03		0.06		0.05		0.08		0.05		0.04	
MSE bond angle			-1.0		1.0		3.0		1.7		-2.5		1.6		1.4	
MUE bond angle			2.6		1.8		3.9		2.5		8.5		5.4		3.7	
Compounds Containing Ti, Cu, Zr and Mo.																
TiBr	Br-Ti	2.35	2.21	-0.14									2.33	-0.02	2.35	0.00
CuBr	Br-Cu	2.29	2.27	-0.01									2.13	-0.16	2.13	-0.16
ZrBr	Br-Zr	2.55	2.42	-0.13									2.67	0.12	2.39	-0.16
MoBr	Br-Mo	2.45	2.45	0.00									2.44	-0.01	2.47	0.02
			AM1*										**PM5**		**PM6**	
MSE bond length			-0.07										-0.02		-0.07	
MUE bond length			0.07										0.08		0.08	

published [35] we have also compared our results with this method.

AM1* can be seen to reproduce heats of formation for the training set of bromine compounds (excluding compounds of Ti, Cu, Zr and Mo, which are available only in AM1*, PM5 and PM6) slightly better than PM3, PM5 or PM6, far better than MNDO and AM1, and slightly worse than MNDO/d. These results are roughly what we expect, as AM1* uses the unchanged AM1 parameterization for the elements H, C, N, O and F, which limits the possible accuracy of the parameterization. This interpretation is partly justified by the relatively large negative AM1* error (−10.9 kcal mol⁻¹) for BrOH and for the large negative errors found for BrF (−13.4 kcal mol⁻¹), CBrClF₂ (−26.0 kcal mol⁻¹), and the very large positive error (+68.4 kcal mol⁻¹) for BrFO₃. It does not, however, explain the large negative errors for Br₂S₂ (−15.5 kcal mol⁻¹) BrSi and Br₃Si (−12.3 and −13.0 kcal mol⁻¹, respectively) and

the phosphorus anion Br₃P⁻ (−17.0) and the large positive error (+39.6 kcal mol⁻¹) for Br₃P = O. With the exception of the oxygen in Br₃P = O, these compounds contain only "pure" AM1* elements. We note, however, that all methods give negative errors for Br₄P⁻. A particularly annoying example, however, is ZnBr₂, for which AM1* gives an error of 49.4 kcal mol⁻¹. This error represents a necessary compromise in the parameterization as the Zn–Br bond length is also in error by 0.11 Å. Quite generally, we find disappointing results for compounds that contain two or more "pure" AM1* elements. This is likely to be a consequence of our sequential parameterization strategy, in contrast to the simultaneous parameterization used for PM6, [35] aggravated by using the original AM1 parameters for H, C, N, O and F. Nevertheless, on aggregate, AM1* performs at the level expected of a modern NDDO-based technique for the heats of formation of bromine compounds.

Table 5 Calculated AM1*, MNDO/d, MNDO, AM1, PM3, PM5 and PM6 heats of formation and errors compared with our target values for the iodine compounds used to parameterize AM1* (all values kcal mol^{-1}). Errors are classified by coloring the boxes in which they appear. *Green* indicates errors lower than 10 kcal mol^{-1}, *yellow* 10–20 kcal mol and *pink* those greater than 20 kcal mol^{-1}

Compound	Target	AM1*		MNDO/d		MNDO		AM1		PM3		PM5		PM6	
		ΔH°f	Error	ΔH°f	Error	ΔH°f	Error	ΔH°f	Error	ΔH°f	Error	ΔH°f	Error	ΔH°f	Error
I	25.5	25.5	0.0	25.5	0.0	25.5	0.0	25.5	0.0	25.5	0.0	25.5	0.0	25.5	0.0
I$^+$	266.6	256.3	-10.3	239.3	-27.3	271.8	5.2	267.7	1.0	238.0	-28.6	257.8	-8.8	258.2	-8.4
I$^-$	-44.9	-49.2	-4.3	-45.0	-0.1	-6.4	38.5	-2.2	42.7	-64.6	-19.7	-46.5	-1.6	-43.1	1.8
I$_2$	14.9	7.6	-7.3	24.2	9.3	21.2	6.3	19.8	4.9	20.7	5.8	5.0	-9.9	16.6	1.7
IH	6.3	6.7	0.4	22.8	16.5	15.7	9.4	7.9	1.6	28.8	22.5	-2.2	-8.5	2.1	-4.2
CH$_3$I	3.5	8.9	5.4	4.6	1.1	1.9	-1.6	5.7	2.2	9.4	5.9	7.6	4.1	7.5	4.0
CH$_2$I$_2$	28.0	24.1	-3.9	22.9	-5.1	16.8	-11.2	21.5	-6.5	33.5	5.5	27.1	-0.9	29.7	1.7
CHI$_3$	50.4	36.8	-13.6	41.6	-8.8	32.0	-18.4	37.8	-12.6	60.6	10.2	47.3	-3.1	54.3	3.9
CI$_4$	62.4	46.6	-15.8	60.7	-1.7	46.8	-15.6	54.2	-8.2	100.8	38.4	68.0	5.6	82.1	19.7
C$_2$H$_5$I	-1.8	-1.8	0.0	-2.8	-1.0	-4.5	-2.7	-1.1	0.7	2.1	3.9	0.4	2.2	1.3	3.1
CH$_2$I-CH$_2$I	17.5	11.1	-6.4	15.1	-2.4	11.5	-6.0	15.7	-1.8	23.3	5.8	14.3	-3.2	18.3	0.8
CHI=CH$_2$	31.0	35.9	4.9	28.5	-2.5	24.5	-6.5	29.8	-1.2	35.2	4.2	31.6	0.6	31.6	0.6
CHI=CHI cis	49.6	52.4	2.8	43.6	-6.0	35.1	-14.5	43.5	-6.1	62.8	13.2	46.5	-3.1	49.2	-0.4
CHI=CHI trans	49.6	53.2	3.6	42.8	-6.8	35.2	-14.4	44.1	-5.5	55.0	5.4	47.4	-2.2	47.9	-1.7
1-C$_3$H$_7$I	-7.2	-8.4	-1.2	-6.8	0.4	-8.8	-1.6	-7.2	0.0	-0.6	6.6	-5.0	2.2	-4.0	3.2
2-C$_3$H$_7$I	-9.6	-10.5	-0.9	-7.1	2.5	-7.5	2.1	-5.7	3.9	-5.3	4.3	-7.3	2.3	-6.7	2.9
1,2-C$_3$H$_6$I$_2$	8.5	4.6	-3.9	12.2	3.7	9.7	1.2	12.0	3.5	18.6	10.1	13.3	4.8	10.6	2.1
(CH$_2$I)HC=CH$_2$	21.9	22.2	0.3	20.8	-1.1	19.5	-2.4	22.4	0.5	27.2	5.3	23.8	1.9	22.9	1.0
(CH$_3$)HC=CHI (E)	22.3	26.3	4.0	18.7	-3.6	14.5	-7.8	19.7	-2.6	25.4	3.1	23.3	1.1	21.2	-1.1
(CH$_3$)HC=CHI (Z)	20.7	25.8	5.1	19.5	-1.2	15.3	-5.4	20.5	-0.2	29.2	8.5	23.4	2.7	21.2	0.5
1,2-C$_4$H$_8$I$_2$	2.9	-5.2	-8.1	9.5	6.6	6.1	3.2	5.6	2.7	22.2	19.3	2.6	-0.3	7.3	4.4
C(CH$_3$)$_3$I	-17.2	-17.2	0.0	-7.7	9.5	-6.5	10.7	-8.3	8.9	-12.5	4.7	-15.2	2.0	-15.8	1.4
C$_6$H$_5$I	39.4	41.0	1.6	35.8	-3.6	32.5	-6.9	38.1	-1.3	44.7	5.3	40.3	0.9	40.0	0.6
cyclo-C$_6$H$_{11}$I	-11.9	-24.1	-12.2	-16.0	-4.1	-17.0	-5.1	-20.0	-8.1	-11.7	0.2	-19.6	-7.7	-13.7	-1.8
o-C$_6$H$_4$I$_2$	60.2	58.1	-2.1	52.0	-8.2	44.8	-15.4	54.0	-6.2	73.8	13.6	56.5	-3.7	58.3	-1.9
C$_6$H$_5$-CH$_2$I	25.0	27.6	2.6	30.2	5.2	28.7	3.7	30.9	5.9	37.6	12.6	30.1	5.1	32.0	7.0
o-I-C$_6$H$_4$-CH$_3$	31.7	32.9	1.2	30.1	-1.6	27.0	-4.7	31.9	0.2	38.9	7.2	32.5	0.8	30.1	-1.6
m-I-C$_6$H$_4$-CH$_3$	31.9	33.4	1.5	28.1	-3.8	24.8	-7.1	30.5	-1.4	35.4	3.5	32.1	0.2	29.9	-2.0
p-I-C$_6$H$_4$-CH$_3$	28.9	33.5	4.6	28.0	-0.9	24.7	-4.2	30.4	1.5	35.4	6.5	32.1	3.2	29.8	0.9
1-I-naphthalene	55.9	59.1	3.2	55.1	-0.8	52.0	-3.9	58.5	2.6	66.0	10.1	56.7	0.8	56.8	0.9
2-I-naphthalene	56.2	59.4	3.2	52.9	-3.3	49.6	-6.6	56.8	0.6	61.9	5.7	55.8	-0.4	56.1	-0.1
IO	41.8	41.2	-0.6	39.7	-2.1	46.7	4.9	37.0	-4.8	31.0	-10.8	35.8	-6.0	41.1	-0.7
CH$_3$COI	-30.2	-21.6	8.6	-26.6	3.6	-26.9	3.3	-20.7	9.5	-29.9	0.3	-27.9	2.3	-30.2	0.0
CH$_3$COCH$_2$I	-31.2	-34.8	-3.6	-28.2	3.0	-30.5	0.7	-29.1	2.1	-26.3	4.9	-33.7	-2.5	-34.5	-3.3
C$_6$H$_5$-COI	2.5	11.4	8.9	5.8	3.3	5.1	2.6	14.1	11.6	8.0	5.5	5.0	2.5	6.5	4.0
p-I-C$_6$H$_4$-COOH	-54.5	-49.6	4.9	-52.3	2.2	-55.6	-1.1	-50.9	3.6	-44.4	10.1	-49.7	4.8	-47.5	7.0
ICN	53.7	50.5	-3.2	49.0	-4.7	39.6	-14.1	42.6	-11.1	63.5	9.8	49.4	-4.3	54.0	0.3
INO	26.8	26.8	0.0	20.0	-6.8	20.9	-5.9	32.3	5.5	18.2	-8.6	25.9	-0.9	26.2	-0.6
IF	-22.7	-27.3	-4.6	-28.4	-5.7	-9.3	13.4	-9.1	13.6	-8.0	14.7	-14.2	8.5	-32.7	-10.0
IF$_5$	-200.7	-205.1	-4.4	-198.3	2.4	97.9	298.6	67.0	267.7	-201.1	-0.4	-157.7	43.0	-207.9	-7.2
IF$_7$	-229.7	-229.6	0.1	-228.0	1.7	236.1	465.8	193.3	423.0	-12.2	217.5	-179.5	50.2	-222.4	7.3
CF$_3$I	-140.5	-153.0	-12.5	-133.2	7.3	-128.2	12.3	-132.6	7.9	-137.9	2.6	-136.1	4.4	-141.1	-0.6
ICl	4.2	-11.9	-16.1	0.5	-3.7	-6.9	-11.1	-4.6	-8.8	10.8	6.6	-6.8	-11.0	3.0	-1.2
ICl$^-$	-51.4	-60.0	-8.6	0.5	51.9	-6.9	44.5	-4.6	46.8	10.8	62.2	-78.8	-27.4	-76.4	-25.0
ICl$_2^-$	-94.0	-79.8	14.2	28.6	122.6	0.5	94.5	3.0	97.0	-55.7	38.3	-109.7	-15.7	-95.0	-1.0
ICl$_4^-$	-150.8	-150.9	-0.1	62.0	212.8	-18.6	132.3	-16.3	134.5	-64.4	86.4	-128.3	22.6	-98.4	52.4
Cl-CH$_2$-CH$_2$-I	-11.4	-9.7	1.7	-7.8	3.6	-12.4	-1.0	-9.0	2.4	-0.3	11.1	-8.8	2.6	-5.7	5.7
IAl	16.2	66.0	49.8	25.3	9.1	31.2	15.0	29.0	12.8	11.9	-4.3	25.5	9.3	18.4	2.2
AlI$_3$	-46.2	39.3	85.5	-47.3	-1.1	11.6	57.8	-29.7	16.5	-22.1	24.1	-38.2	8.0	-46.4	-0.2
Al$_2$I$_6$	-117.0	-117.0	0.0	-126.0	-9.0	7.5	124.5	-107.9	9.1	-59.1	57.9	-118.9	-1.9	-119.2	-2.2
SiI	76.4	76.3	-0.1	71.3	-5.1	107.9	31.5	92.2	15.8	68.5	-7.9	67.3	-9.1	68.8	-7.6
SiI$_2$	22.0	20.9	-1.1	38.9	16.9	82.1	60.1	57.5	35.5	18.0	-4.0	19.3	-2.7	29.4	7.4
SiI$_3$	8.4	8.5	0.0	24.4	15.9	43.6	35.2	9.6	1.1	-50.3	-58.7	-8.9	-17.3	1.1	-7.3

Table 5 (continued)

Compound	Target	AM1* ΔH°f	Error	MNDO/d ΔH°f	Error	MNDO ΔH°f	Error	AM1 ΔH°f	Error	PM3 ΔH°f	Error	PM5 ΔH°f	Error	PM6 ΔH°f	Error
SiI_4	-26.4	-35.6	-9.2	4.0	30.4	42.4	68.8	1.6	28.0	-14.2	12.2	-27.1	-0.7	-16.9	9.5
$SiIH_3$	-0.5	21.0	21.5	10.1	10.6	11.0	11.5	4.9	5.4	3.1	3.6	1.9	2.4	2.3	2.8
SiI_2H_2	-9.1	8.9	18.0	10.5	19.6	23.0	32.1	5.0	14.1	-3.5	5.6	-6.7	2.4	-3.8	5.3
SiI_3H	-17.8	-11.1	6.7	8.8	26.6	34.1	51.9	3.9	21.7	-9.0	8.8	-16.3	1.5	-10.6	7.2
IP	64.8	59.5	-5.3	59.6	-5.2	61.6	-3.2	56.2	-8.6	55.9	-9.0	42.0	-22.8	28.7	-36.1
I_2P	57.5	34.8	-22.7	32.6	-24.9	34.9	-22.6	34.2	-23.3	-9.2	-66.7	12.1	-45.5	-16.0	-73.5
I_3P	1.1	1.1	0.0	20.4	19.3	25.3	24.2	24.4	23.3	38.8	37.7	-13.4	-14.5	-57.3	-58.4
IOP	-30.8	-20.1	10.7	-35.9	-5.1	-24.6	6.2	-15.7	15.1	-43.6	-12.8	-26.6	4.2	-49.0	-18.1
IS^-	11.2	11.2	0.0	-21.0	-32.2	-10.0	-21.2	-19.8	-31.0	-25.6	-36.8	-43.5	-54.7	-39.7	-50.9
I_2S	61.8	61.1	-0.7	24.2	-37.6	29.6	-32.3	21.7	-40.1	51.6	-10.2	12.2	-49.6	19.3	-42.5
C_2H_5SI	6.4	13.1	6.7	10.0	3.6	-1.7	-8.1	6.4	0.0	13.8	7.4	10.8	4.4	13.4	7.0
ZnI_2	-15.6	88.2	103.8	0.2	15.8	42.7	58.3	4.7	20.3	15.7	31.3	-2.1	13.5	-15.9	-0.3
ZnI_4^{2-}	-99.0	-99.0	-0.1	-183.5	-84.5	-2.6	96.4	-68.1	30.8	-152.0	-53.0	-119.8	-20.8	-112.0	-13.1
BrI	9.8	2.4	-7.4	12.4	2.6	7.2	-2.5	6.0	-3.8	15.7	5.9	-2.0	-11.8	9.6	-0.1
BrI^-	-49.0	-49.0	0.0	-53.9	-4.9	-53.2	-4.2	-43.1	5.9	-104.2	-55.2	-76.6	-27.6	-75.1	-26.1
Br_2I^-	-60.0	-85.7	-25.7	-72.4	-12.4	-84.9	-24.9	-70.9	-10.9	-84.5	-24.5	-120.0	-60.0	-104.1	-44.1
$HBrI^-$	-69.8	-57.6	12.3	-32.4	37.5	-39.9	29.9	-33.0	36.8	-43.4	26.5	-94.4	-24.6	-67.5	2.3
CH_3BrI^-	-62.5	-56.2	6.3	-51.6	10.9	-44.8	17.7	-34.1	28.4	-65.6	-3.1	-76.3	-13.8	-70.1	-7.6

		AM1*		MNDO/d		MNDO		AM1		PM3		PM5		PM6	
Most positive error		103.8		212.8		465.8		423.0		217.5		50.2		52.4	
Most negative error		-25.7		-84.5		-32.3		-40.1		-66.7		-60.0		-73.5	
MSE		2.6		4.9		22.0		17.3		7.4		-3.8		-3.9	
MUE		8.7		14.5		30.8		23.0		19.1		10.2		9.1	
RMSD		18.8		33.6		74.1		64.4		35.5		17.4		17.8	

Compounds Containing Ti, Cu, Zr and Mo.

Compound	Target	AM1* ΔH°f	Error	PM5 ΔH°f	Error	PM6 ΔH°f	Error
TiI	66.0	24.2	-41.8	11.0	-55.0	30.8	-35.2
TiI_2	-5.0	-1.9	3.1	-27.0	-22.0	0.8	5.8
TiI_3	-43.0	17.7	60.7	-42.7	0.3	-31.7	11.3
TiI_4	-66.0	-3.1	63.0	-62.4	3.6	-49.0	17.0
CuI	43.5	43.2	-0.3	44.1	0.6	25.7	-17.8
CuI_2	32.0	53.9	21.9	-1.9	-33.9	13.9	-18.1
ZrI	92.0	37.5	-54.5	65.6	-26.4	76.0	-16.0
ZrI_2	21.0	20.4	-0.6	-15.8	-36.8	-4.0	-25.0
ZrI_3	-35.0	19.7	54.7	-49.7	-14.7	-55.3	-20.3
ZrI_4	-87.0	26.4	113.4	-95.8	-8.8	-86.4	0.6
MoI	119.2	157.5	38.3	187.5	68.3	135.4	16.2
MoI_2	61.6	101.6	40.0	131.4	69.8	97.2	35.6
MoI_3	43.7	44.9	1.2	46.2	2.5	38.2	-5.5
MoI_4	29.8	26.6	-3.2	30.7	0.9	19.3	-10.5

	AM1*	PM5	PM6
Most positive error	113.4	69.8	35.6
Most negative error	-54.5	-55.0	-35.2
MSE	21.1	-3.7	-4.4
MUE	35.5	24.5	16.8
RMSD	47.7	34.4	19.4

Ionization potentials and dipole moments

Table 3 shows a comparison of the calculated and experimental ionization potentials and dipole moments.

AM1* underestimates ionization potentials of the test set of bromine compounds by about 0.07 eV. The AM1* MUE is only slightly worse than MNDO/d and AM1, and is better than MNDO or PM3. In this respect, PM5 and PM6

perform by far the best of the methods investigated. We note, however, that all the large AM1* errors (−1.03, −1.55 and −1.58 eV for BrF, BrF$_3$ and CBrF$_2$–CBrF$_2$, respectively) are given by fluorine-containing compounds, and so may be an indirect result of the original AM1 parameterization for fluorine.

Both AM1* and MNDO/d tend to overestimate dipole moments for the bromine compounds in the training set slightly (by 0.1–0.2 Debye). The mean unsigned errors vary over a relatively small range from 0.24 (MNDO/d) to 0.52 (PM5). The AM1* value of 0.35 Debye lies in the middle

of this range. AM1* seriously overestimates the dipole moment of SiH$_3$Br and BrF$_3$.

Geometries

Table 4 shows the performance of the different methods in reproducing the geometries (bond lengths and angles) of bromine-containing compounds. MNDO and PM3 underestimate bond lengths to bromine systematically, as does AM1*. The AM1* mean signed error is, however, only

Table 6 Calculated AM1*, MNDO/d, MNDO, AM1, PM3, PM5 and PM6 Koopmans' theorem ionization potentials and dipole moments for iodine-containing compounds. The errors are color coded as follows: *green* up to 0.5 eV or 0.5 Debye; *yellow* between 0.5 and 1.0; *pink* larger than 1.0

Compound	Target	AM1*	Error	MNDO/d	Error	MNDO	Error	AM1	Error	PM3	Error	PM5	Error	PM6	Error
Koopmans' Theorem Ionization Potentials for Iodine Compounds (eV)															
IH	10.39	9.42	-0.97	9.56	-0.83	11.21	0.82	10.91	0.52	9.97	-0.42	10.39	0.00	10.19	-0.21
CH$_3$I	9.54	9.29	-0.25	9.38	-0.16	10.85	1.31	10.51	0.97	9.47	-0.07	9.83	0.29	9.88	0.34
CH$_2$I$_2$	9.46	9.09	-0.37	9.44	-0.02	10.87	1.41	10.56	1.10	8.98	-0.48	9.40	-0.06	9.75	0.29
C$_2$H$_5$I	9.34	9.27	-0.07	9.34	0.00	10.81	1.47	10.43	1.09	9.44	0.10	9.72	0.38	9.72	0.38
CH$_2$I-CH$_2$I	9.50	8.67	-0.83	9.59	0.09	11.02	1.52	10.71	1.21	9.66	0.16	9.88	0.38	10.05	0.55
1-C$_3$H$_7$I	9.27	9.28	0.01	9.33	0.06	10.80	1.53	10.39	1.12	9.42	0.15	9.74	0.47	9.74	0.47
2-C$_3$H$_7$I	9.40	9.26	-0.14	9.30	-0.10	10.79	1.39	10.40	1.00	9.43	0.03	9.63	0.23	9.57	0.17
C$_6$H$_5$I	8.78	9.03	0.25	8.89	0.11	9.55	0.77	9.65	0.87	9.04	0.26	9.30	0.52	9.41	0.63
cyclo-C$_6$H$_{11}$I	8.91	9.26	0.35	9.28	0.37	10.77	1.86	10.38	1.47	9.42	0.51	9.64	0.73	9.59	0.68
C$_6$H$_5$-CH$_2$I	8.91	8.70	-0.21	9.20	0.29	9.46	0.55	9.51	0.60	9.35	0.44	9.10	0.19	9.32	0.41
o-I-C$_6$H$_4$-CH$_3$	8.53	8.96	0.43	8.90	0.37	9.51	0.98	9.52	0.99	9.02	0.49	9.21	0.68	9.29	0.76
m-I-C$_6$H$_4$-CH$_3$	8.55	8.95	0.40	8.89	0.34	9.51	0.96	9.52	0.97	9.01	0.46	9.19	0.64	9.32	0.77
p-I-C$_6$H$_4$-CH$_3$	8.38	8.87	0.49	8.87	0.49	9.45	1.07	9.41	1.03	8.94	0.56	9.08	0.70	9.17	0.79
CF$_3$I	10.45	10.24	-0.21	10.40	-0.05	12.48	2.03	11.97	1.52	10.28	-0.17	11.35	0.90	11.01	0.56
AlI$_3$	9.66	8.17	-1.49	9.88	0.22	10.98	1.32	10.94	1.28	9.91	0.25	9.97	0.31	9.95	0.29
ICl	10.10	9.75	-0.35	9.70	-0.40	11.58	1.48	11.12	1.02	9.74	-0.36	10.34	0.24	10.26	0.16
ZnI$_2$	9.73	8.40	-1.33	9.45	-0.28	10.62	0.89	10.49	0.76	10.26	0.53	10.03	0.30	10.16	0.43
BrI	9.85	10.02	0.17	9.75	-0.10	11.28	1.43	10.84	0.99	9.84	-0.01	10.28	0.43	10.18	0.33
I$_2$	9.34	9.46	0.12	9.57	0.23	10.87	1.53	10.67	1.33	9.53	0.19	9.87	0.53	9.73	0.39
MSE			-0.21		0.03		1.28		1.04		0.14		0.41		0.43
MUE			0.44		0.24		1.28		1.04		0.30		0.42		0.45
Dipole Moments for Iodine Containing Compounds (Debye)															
IH	0.45	1.83	1.38	0.93	0.48	1.01	0.56	1.27	0.82	0.97	0.52	0.43	-0.02	1.08	0.63
CH$_3$I	1.65	1.63	-0.02	1.80	0.15	1.37	-0.28	1.35	-0.30	1.44	-0.21	1.17	-0.48	1.22	-0.44
CH$_2$I$_2$	1.62	1.88	0.26	1.41	-0.21	1.15	-0.47	1.12	-0.50	1.20	-0.42	0.74	-0.88	0.97	-0.65
C$_2$H$_5$I	1.91	1.49	-0.42	1.92	0.01	1.42	-0.49	1.50	-0.41	1.83	-0.08	1.68	-0.23	1.88	-0.03
1-C$_3$H$_7$I	2.04	1.51	-0.53	1.92	-0.12	1.42	-0.62	1.51	-0.53	1.81	-0.23	1.64	-0.41	1.89	-0.15
C$_6$H$_5$I	1.70	2.51	0.81	1.79	0.09	1.60	-0.10	1.43	-0.27	0.79	-0.91	0.94	-0.76	1.63	-0.07
IF	1.95	4.16	2.21	2.29	0.34	2.18	0.23	1.65	-0.30	2.59	0.64	3.87	1.92	1.93	-0.02
CF$_3$I	1.04	5.89	4.85	1.85	0.81	2.14	1.10	1.67	0.63	1.55	0.51	3.09	2.05	1.50	0.46
ICl	1.24	5.51	4.27	1.26	0.02	1.34	0.10	0.95	-0.29	0.48	-0.76	2.25	1.01	1.20	-0.04
BrI	0.74	5.82	5.08	0.91	0.17	0.72	-0.02	0.63	-0.11	0.53	-0.21	1.50	0.76	0.72	-0.02
MSE			1.79		0.17		0.00		-0.13		-0.12		0.30		-0.03
MUE			1.98		0.24		0.40		0.42		0.45		0.85		0.25

Table 7 Calculated AM1*, MNDO/d, MNDO, AM1, PM3, PM5 and PM6 bond lengths and angles for iodine-containing compounds. The errors are color coded as follows: *green* up to 0.05 Å or 0.5°; *yellow* between 0.05 and 0.1 Å or 0.5–1.0°; *pink* larger than 0.1 Å or 1°

Compound	Variable	Target	AM1*	Error	MNDO/d	Error	MNDO	Error	AM1	Error	PM3	Error	PM5	Error	PM6	Error
IH	I-H	1.61	1.61	0.00	1.59	-0.01	1.57	-0.04	1.59	-0.02	1.68	0.07	1.21	-0.40	1.64	0.03
CH3I	I-C	2.14	2.16	0.02	2.08	-0.05	2.02	-0.12	2.05	-0.09	2.03	-0.11	2.16	0.02	2.13	-0.01
	I-C-H	107.5	105.4	-2.1	109.0	1.5	110.5	3.0	109.2	1.7	109.1	1.6	106.7	-0.8	109.2	1.7
CHI3	I-C	2.12	2.13	0.01	2.08	-0.04	2.01	-0.12	2.04	-0.08	1.96	-0.16	2.10	-0.02	2.13	0.01
	I-C-I	113.0	107.9	-5.1	111.4	-1.6	111.6	-1.4	111.1	-1.9	97.5	-15.5	106.9	-6.1	113.2	0.2
C2H5I	I-C	2.14	2.17	0.04	2.10	-0.04	2.03	-0.11	2.07	-0.07	2.04	-0.10	2.18	0.04	2.18	0.04
	I-C-C	112.2	108.4	-3.8	112.5	0.3	115.0	2.8	113.5	1.3	106.3	-5.9	107.5	-4.7	112.2	0.0
(CH2I)HC=CH2	I-C	2.19	2.17	-0.02	2.10	-0.09	2.03	-0.16	2.07	-0.12	2.04	-0.15	2.18	-0.01	2.17	-0.02
	I-C-C	107.6	112.0	4.4	110.5	2.9	112.9	5.3	111.4	3.8	106.9	-0.7	113.4	5.8	116.9	9.3
C6H5I	I-C	2.08	2.15	0.07	2.03	-0.05	1.98	-0.11	2.02	-0.06	1.97	-0.11	2.09	0.01	2.12	0.04
CH3COI	I-C	2.22	2.21	-0.01	2.11	-0.11	2.04	-0.18	2.09	-0.13	2.05	-0.17	2.18	-0.04	2.21	-0.01
	I-C-C	111.8	112.7	0.9	113.1	1.3	114.4	2.6	113.1	1.3	106.9	-4.9	106.2	-5.6	109.9	-1.9
	I-C=O	119.4	119.5	0.1	120.3	0.9	122.9	3.5	123.4	4.0	120.8	1.4	122.1	2.7	121.3	1.9
ICN	I-C	1.99	2.15	0.16	1.94	-0.05	1.89	-0.10	1.93	-0.06	1.91	-0.08	1.98	-0.01	2.02	0.03
INO	I-N	2.30	2.27	-0.03	2.14	-0.16	2.06	-0.24	2.08	-0.23	1.96	-0.34	2.14	-0.16	1.92	-0.38
	I-N-O	120.6	116.1	-4.5	119.2	-1.4	121.7	1.1	123.1	2.5	124.6	4.0	127.7	7.1	133.3	12.7
IO	I-O	1.87	1.99	0.12	1.89	0.02	1.89	0.02	1.90	0.03	1.86	-0.01	1.91	0.04	1.97	0.10
CF3I	I-C	2.14	2.26	0.11	2.16	0.01	2.13	-0.02	2.18	0.03	2.05	-0.09	2.22	0.07	2.15	0.01
IF	I-F	1.91	1.91	0.00	1.95	0.04	1.90	-0.01	1.88	-0.03	1.89	-0.02	1.88	-0.03	1.92	0.01
IF5	I-Fax	1.81	1.92	0.11	1.93	0.12	1.98	0.17	1.93	0.12	1.87	0.06	1.95	0.14	1.91	0.10
	I-Feq	1.87	1.91	0.03	1.96	0.08	1.96	0.09	1.90	0.03	1.88	0.01	1.30	-0.57	1.84	-0.03
	Fax-I-Feq	83.0	89.9	6.9	82.3	-0.7	78.1	-4.9	77.3	-5.7	102.5	19.5	94.4	11.4	90.0	7.0
IF7	I-Fax	1.79	1.90	0.12	1.91	0.12	1.98	0.19	1.93	0.15	1.88	0.10	1.79	0.00	1.84	0.05
	I-Feq	1.86	1.92	0.06	1.95	0.09	2.03	0.17	1.97	0.11	1.92	0.06	1.88	0.02	1.92	0.06
O=IF5	I-Fax	1.86	1.91	0.04	1.93	0.06	2.00	0.14	1.96	0.09	1.87	0.01	1.26	-0.61	1.79	-0.08
	I-Feq	1.82	1.89	0.08	1.92	0.11	1.97	0.15	1.92	0.10	1.88	0.07	1.22	-0.60	1.77	-0.05
	I=O	1.72	2.09	0.38	1.78	0.07	2.19	0.47	2.06	0.34	2.86	1.15	2.39	0.68	1.67	-0.05
	O=I-Feq	98.0	90.4	-7.6	97.7	-0.3	101.5	3.5	101.5	3.5	86.9	-11.1	75.0	-23.0	96.7	-1.3
ICl	I-Cl	2.32	2.32	0.00	2.31	-0.01	2.26	-0.06	2.22	-0.10	2.19	-0.13	2.33	0.01	2.34	0.02
IBr	I-Br	2.49	2.43	-0.06	2.46	-0.03	2.35	-0.14	2.35	-0.13	2.56	0.08	2.45	-0.04	2.49	0.00
I2	I-I	2.67	2.64	-0.03	2.64	-0.03	2.52	-0.15	2.54	-0.13	2.67	0.00	2.63	-0.04	2.57	-0.09
AlI	I-Al	2.54	2.71	0.17	2.47	-0.06	2.36	-0.18	2.42	-0.12	2.47	-0.07	2.43	-0.11	2.59	0.06
AlI3	I-Al	2.50	2.58	0.08	2.39	-0.11	2.33	-0.17	2.39	-0.11	2.61	0.11	2.37	-0.13	2.49	-0.01
Al2I6	I-Al	2.45	2.49	0.04	2.39	-0.06	2.34	-0.11	2.40	-0.05	2.63	0.18	2.37	-0.08	2.50	0.05
SiI	I-Si	2.44	2.74	0.30	2.42	-0.02	3.31	0.87	2.27	-0.17	1.92	-0.52	2.16	-0.28	2.37	-0.07
SiI4	I-Si	2.43	2.52	0.09	2.40	-0.03	2.33	-0.10	2.43	-0.01	2.47	0.04	2.43	0.00	2.40	-0.03
SiIH3	I-Si	2.44	2.57	0.14	2.44	0.01	2.39	-0.05	2.43	0.00	2.01	-0.42	2.48	0.05	2.45	0.01
	Si-H	1.49	1.44	-0.05	1.41	-0.08	1.37	-0.12	1.47	-0.02	1.49	0.01	1.37	-0.12	1.49	0.00
	I-Si-H	107.8	108.8	1.0	107.4	-0.4	108.4	0.6	109.8	2.0	107.9	0.1	106.9	-0.9	109.6	1.8
IPO	I-P	2.69	2.55	-0.14	2.41	-0.28	2.30	-0.39	2.30	-0.39	2.43	-0.26	2.43	-0.26	2.55	-0.14
I3P	I-P	2.46	2.50	0.04	2.37	-0.09	2.26	-0.20	2.25	-0.21	2.36	-0.10	2.40	-0.06	2.52	0.06
IS⁻	I-S	2.66	2.56	-0.11	2.30	-0.36	2.22	-0.44	2.30	-0.36	2.86	0.20	2.38	-0.28	2.39	-0.27
I2S	I-S	2.59	2.67	0.08	2.34	-0.25	2.24	-0.35	2.33	-0.26	2.20	-0.39	2.30	-0.29	2.38	-0.21
ZnI2	I-Zn	2.53	2.53	0.00	2.23	-0.30	2.38	-0.15	2.35	-0.18	2.40	-0.13	2.40	-0.13	2.35	-0.18
			AM1*		MNDO/d		MNDO		AM1		PM3		PM5		PM6	
MSE bond length			0.05		-0.05		-0.05		-0.06		-0.04		-0.09		-0.03	
MUE bond length			0.08		0.09		0.18		0.12		0.16		0.16		0.07	
MSE bond angle			-1.0		0.3		1.6		1.3		-1.2		-1.4		3.2	
MUE bond angle			3.6		1.1		2.9		2.8		6.5		6.8		3.8	

Table 7 (continued)

Compound	Variable	Target	AM1*		MNDO/d	MNDO	AM1	PM3	PM5		PM6	
				Error	Error	Error	Error	Error		Error		Error
Compounds Containing Ti, Cu, Zr and Mo.												
TiI₂	I-Ti	2.63	2.63	0.00					2.73	0.11	2.60	-0.03
CuI	I-Cu	2.44	2.42	-0.02					2.34	-0.10	2.36	-0.08
CuI₂	I-Cu	2.48	2.50	0.01					2.31	-0.18	2.51	0.03
ZrI₂	I-Zr	2.77	2.67	-0.10					2.90	0.13	2.76	-0.01
MoI	I-Mo	2.63	2.48	-0.15					2.69	0.06	1.96	-0.67
			AM1*						**PM5**		**PM6**	
MSE bond length			-0.05						0.00		-0.15	
MUE bond length			0.06						0.11		0.16	

0.02 Å. MNDO/d and PM6 give the smallest mean unsigned errors for bond lengths (0.03 and 0.04 Å, respectively) and PM3 the largest (0.08 Å). The other four methods, including AM1*, give mean unsigned errors of 0.05–0.06 Å.

PM3 systematically underestimates bond angles to bromine (by 2.5°), as does AM1* (but only by 1.0°). The other methods all systematically overestimate these angles with mean signed errors between 1.0° (MNDO/d) and 3.0° (MNDO). MNDO/d gives the lowest mean unsigned error (1.8°) followed by AM1* and AM1 (2.6°). PM3 gives by far the largest mean unsigned error (8.5°).

Iodine

Heats of formation

The results obtained for heats of formation of iodine compounds are shown in Table 5.

Table 5 shows clearly that the three newest methods, AM1*, PM5 and PM6, give the best results. They perform very similarly, with mean unsigned errors ranging from 8.7 to 10.2 kcal mol⁻¹. PM5 and PM6 give slightly too negative heats of formation, with mean signed errors of −3.8 and −3.9 kcal mol⁻¹, respectively, whereas AM1* deviates slightly less (2.6 kcal mol⁻¹) in the opposite direction. Large AM1* errors are found for CI₄ (−15.8 kcal mol⁻¹), mononuclear aluminum iodides (+49.8 kcal mol⁻¹ for AlI and +85.5 kcal mol⁻¹ for AlI₃), SiH₃I (+21.5 kcal mol⁻¹) and zinc and bromine iodides (ZnI₂+103.8, Br₂I⁻ −25.7 and HBrI⁻ +12.3 kcal mol⁻¹). Quite generally, AM1* does not do well for poly-halogen compounds but otherwise its performance is acceptable.

Ionization potentials and dipole moments

Table 6 shows a comparison of the calculated and experimental ionization potentials and dipole moments for the training compounds containing iodine.

MNDO and AM1 significantly and systematically over-estimate ionization potentials, but once again the performance of the other methods is comparable. MNDO/d (MUE=0.24 eV) and PM3 (MUE=0.30 eV) perform best, although PM3 tends to overestimate the ionization potentials (MSE=0.14 eV). The three newer methods give comparable mean unsigned errors (0.42, 0.45 and 0.44 eV for PM5, PM6 and AM1*, respectively), although PM5 and PM6 systematically give values that are too high (MSE≈ 0.4 eV), and AM1* yields values that are too low (MSE= −0.21 eV).

AM1* performs very poorly for dipole moments, although the errors are concentrated on compounds containing several halogen atoms and on HI. The dipole moments for these compounds are all seriously overestimated, giving an MUE for AM1* of 1.98 Debye, far larger than any of the other techniques. AM1* cannot, therefore, be recommended for calculating dipole moments of iodine compounds and the molecular electrostatic potential should also be treated with caution, although AM1* usually performs very well in this respect. [36]

Geometries

Table 7 shows the calculated bond lengths and angles to iodine for the training compounds using the different methods.

The mean unsigned errors for calculated bond lengths range from 0.07 Å (PM6) to 0.18 Å (MNDO). AM1* performs relatively well, with an MUE of 0.08 Å. In contrast to all the other methods, AM1* systematically overestimates bond lengths to iodine (MSE=0.05 Å). Surprisingly, the newer methods, PM5, PM6 and AM1*, perform significantly worse for bond angles (MUEs of 3.6, 3.8 and 6.8° for AM1*, PM6 and PM5, respectively) than the older ones (MUEs of 1.1, 2.8 and 2.9° for MNDO/d, AM1 and MNDO, respectively). The exception is PM3, which has an MUE of 6.5°, almost as large as PM5. AM1*

performs differently to PM6 in that the latter systematically overestimates bond angles to iodine (the MSE is +3.2°, compared with the MUE of + 3.8°), whereas AM1* shows almost no strong systematic trend (MSE=−1.0°).

Discussion

The AM1* parameters for bromine and iodine provide important additional elements, both for classical organic chemistry applications and for parameterizing the transition metals, for which data for bromides and iodides are often available. AM1* performs comparably to the more modern of the available methods, and better than those that use only *s*- and *p*-orbital basis sets. Because of the relatively large amount of available experimental data, our parameterization data for Br and I is far more similar to those used for MNDO/d and PM6 than is the case for the transition metals. The similar performances of the different methods are therefore probably not coincidental, but rather reflect the accuracy attainable within the current theoretical framework, which is, for instance, very similar for PM6 and AM1*.

The availability of PM6 and AM1* (and for some elements MNDO/d) as published semiempirical techniques that use *s*-, *p*-, *d*-basis sets and have very similar theoretical frameworks now opens the opportunity to carry out comparison calculations for many applications in order to assess the reliability of the technique for the problem in hand.

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