Thermochemistry of icosahedral closo-dicarboranes: A composite ab initio quantum-chemical perspective

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ABSTRACT

We obtain accurate thermochemical properties for the ortho-, meta-, and para-dicarborane isomers ($C_2B_{10}H_{12}$) by means of explicitly correlated high-level thermochemical procedures. The thermochemical properties include heats of formation, isomerization energies, C–H and B–H bond dissociation energies (BDEs), and ionization potentials. Of these only the ionization potentials are known experimentally. Our best theoretical ionization potentials, obtained by means of the ab initio W1-F12 thermochemical protocol, are: 241.50 (para-dicarborane), 238.45 (meta-dicarborane), and 236.54 (ortho-dicarborane) kcal mol^{-1}. These values agree with the experimental values adopted by the NIST thermochemical tables to within overlapping uncertainties. However, they suggest that the experimental values may represent significant underestimations. For all the isomers the C–H BDEs are systematically higher than the B–H BDEs due to the relative stability of the boron-centered radicals. The C–H BDEs for the three isomers cluster within a narrow energetic interval, namely between 110.8 (para-dicarborane) and 111.7 (meta-dicarborane) kcal mol^{-1}. The B–H BDEs cluster within a larger interval ranging between 105.8 and 108.1 kcal mol^{-1} (both obtained for ortho-dicarborane). We use our benchmark W1-F12 data to assess the performance of a number of lower-cost composite ab initio methods. We find that the Gaussian-3 procedures (G3(MP2)B3 and G3B3) result in excellent performance with overall RMSDs of 0.3–0.4 kcal mol^{-1} for the isomerization, ionization, and bond dissociation energies. However, the Gaussian-4-type procedures (G4, G4(MP2), and G4(MP2)-6X) show relatively poor performance with overall RMSDs of 1.3–3.7 kcal mol^{-1}.

Keywords: Carborane, Computational thermochemistry, CCSD(T), W1-F12 theory.

1. Introduction

Closo (closed) dicarboranes are highly symmetric compounds with the general molecular formula $C_2B_nH_{n+2}$ (n = 3–10). Icosahedral closo-dicarboranes (or simply carboranes hereinafter) are the highest members of this series with the molecular formula of $C_2B_{10}H_{12}$. There are three possible $C_2B_{10}H_{12}$ isomers: *para*-carborane, *meta*-carborane, and *ortho*-carborane (Figure 1).
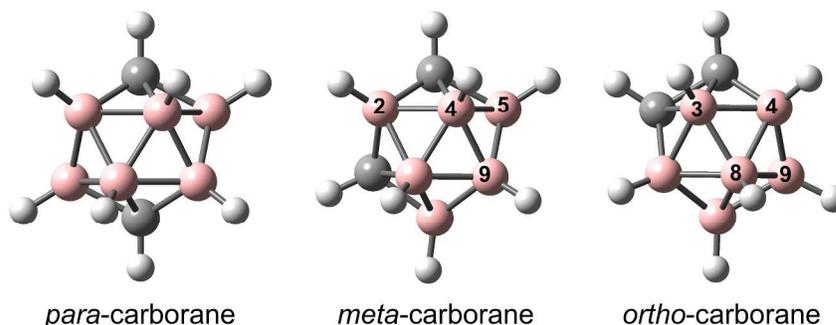

para-carborane   *meta*-carborane   *ortho*-carborane

Figure 1. B3LYP-D3/Def2-TZVPP optimized structures for the $C_2B_{10}H_{12}$ icosahedral carborane isomers having point-group symmetries of D_{5d} (para) and C_{2v} (meta and ortho). Atomic color scheme: H, white; B, pink; C, gray. The IUPAC numbering scheme is displayed for the symmetry unique boron atoms.

These highly symmetric boron-rich cages have attracted a considerable amount of attention ever since *ortho*-carborane was first synthesized more than half a century ago by reacting decaborane with acetylene.[1] Due to their unique chemical properties such as high stability and ease of chemical functionalization, icosahedral carboranes have found potential applications in many fields including catalysis, cancer therapy, drug design, electronic devices, metal–organic frameworks, organometallic synthesis, and polymer functionalization.[1,2,3,4,5,6,7] Nevertheless, many fundamental thermochemical quantities (e.g., heats of formation, and C–H and B–H bond dissociation energies) of the carborane isomers are not well established.

Icosahedral closo-dicarboranes were the subject of extensive theoretical investigations.[8,9,10,11,12,13,14,15] However, there have been only a small number of correlated ab initio investigations of their thermochemical properties. Schleyer and Najafian (SN) calculated the relative stabilities of the para, meta, and ortho isomers at the MP2/6-31G(d) level of theory and found that the meta and ortho isomers lie 3.5 and 19.1 kcal mol^{-1} above the most stable para isomer.[16] Knyazev *et al.*

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calculated the isomerization energies for the carborane isomers at the MP2/6-311+G(d,2p) level of theory.[17] They obtained an isomerization enthalpy of 16.0 kcal mol^{-1} between the ortho and meta isomers. This value was lower than the experimental value of 18.0 ± 3.5 kcal mol^{-1} which was reported in the same work (see ref. 17 for further details). Ten years after the abovementioned investigation by Schleyer and Najafian,[16] Serrano-Andrés *et al.* reported a comprehensive study of the thermodynamic stabilities of carborane mono- and di-radicals using B3LYP, MP2, and CASPT2 calculations.[18] They found that the most stable carborane radicals are derived from dissociations of the hydrogens that are farthest away from the carbon atoms. To the best of our knowledge the thermochemical properties of the $C_2B_{10}H_{12}$ isomers have not been studied at the CCSD(T) level.

One of the goals of the present paper is to reevaluate the stability of the icosahedral dicarborane isomers, their ionization potentials (IPs), and the various C–H and B–H bond dissociation energies (BDEs) by means of the high-level, ab initio W1-F12 thermochemical protocol.[19] W1-F12 is a high-level composite theory which obtains the all-electron, relativistic CCSD(T)/CBS energy (complete basis-set limit coupled cluster with singles, doubles, and quasiperturbative triple excitations) and achieves an accuracy in the sub-kcal mol^{-1} range for molecules whose wavefunctions are dominated by dynamical correlation.[19,20,21]

2. Computational details

In order to obtain accurate thermochemical properties for the $C_2B_{10}H_{12}$ carborane isomers, calculations have been carried out using the high-level, ab initio, W1-F12 procedure with the Molpro 2012.1 program suite.[22] W1-F12 theory combines explicitly correlated F12 techniques[23] with basis-set extrapolations in order to approximate the CCSD(T) basis-set-limit energy. Due to the drastically accelerated basis-set convergence of the F12 methods,[24,25] W1-F12 is superior to the original W1 method[26] in terms of computational cost.[19] For the sake of making the article self-contained, we will briefly outline the various steps in W1-F12 theory (for further details see refs. 19 and 27). The Hartree–Fock component is extrapolated from the VDZ-F12 and VTZ-F12 basis sets, using the $E(L) = E_\infty + A/L^\alpha$ two-point extrapolation formula, with $\alpha = 5$ (where VnZ-F12 denotes the cc-pVnZ-F12 basis sets of Peterson *et al.*,[24] which were specifically developed for explicitly correlated calculations). Note that the complementary auxiliary basis set (CABS) singles correction is included in the SCF energy.[28,29,30] The valence CCSD-F12 correlation energy is extrapolated from the same basis sets, using the $E(L) = E_\infty + A/L^\alpha$ formula, with $\alpha = 3.38$. Optimal values for the geminal Slater exponents (β)

used in conjunction with the VnZ-F12 basis sets were taken from ref. 25. The (T) valence correlation energy is obtained from standard CCSD(T) calculations,[26] namely, extrapolated from the A'VDZ and A'VTZ basis sets using the above two-point extrapolation formula with $\alpha = 3.22$ (where A'VnZ indicates the combination of the standard correlation-consistent cc-pVnZ basis sets on H and the aug-cc-pVnZ basis sets on B and C).[31,32] In all of the explicitly correlated coupled cluster calculations the diagonal, fixed-amplitude 3C(FIX) ansatz,[29,33,34,35] and the CCSD-F12b approximation are employed.[30,36] The CCSD inner-shell contribution is calculated with the core-valence weighted correlation-consistent cc-pwCVTZ basis set of Peterson and Dunning,[37] whilst the (T) inner-shell contribution is calculated with the cc-pwCVTZ(no f) basis set (where cc-pwCVTZ(no f) indicates the cc-pwCVTZ basis set without the f functions). The scalar relativistic contribution (in the second-order Douglas–Kroll–Hess approximation)[38,39] is obtained as the difference between non-relativistic CCSD(T)/A'VDZ and relativistic CCSD(T)/A'VDZ-DK calculations.[40] The diagonal Born–Oppenheimer corrections are calculated at the HF/cc-pVTZ level of theory using the CFOUR program suite.[41] W1-F12 theory can achieve sub-chemical accuracy for atomization reactions. For example, it is associated with a root-mean-square deviation (RMSD) of 0.45 kcal mol^{-1} for a set of 100 very accurate atomization energies of first-row systems.[19,20,21]

The geometries of all structures have been obtained at the B3LYP-D3/Def2-TZVPP level of theory.[42,43,44,45,46] Empirical D3 dispersion corrections[47,48] are included using the Becke−Johnson[49] damping potential as recommended in ref. 45 (denoted by the suffix -D3). Harmonic vibrational frequency analyses have been performed to confirm that all stationary points are equilibrium structures (i.e., they have all real frequencies). Zero-point vibrational energy (ZPVE) and enthalpic corrections have been obtained from such calculations. The ZPVEs were scaled by 0.99 as recommended in refs. 27 and 50. All geometry optimizations and frequency calculations were performed using the Gaussian 09 program suite.[51]

In addition, the performance of more approximate Gaussian-n[52] and CBS-type[53] composite thermochemical procedures is also assessed.[20,54,55] We consider the following composite procedures: G4,[56] G4(MP2),[57] G4(MP2)-6X,[58] G3,[59] G3(MP2),[60] G3B3,[61] G3(MP2)B3,[61] and CBS-QB3.[62,63]

3. Results and discussion

3.1. Multireference considerations. Since W1-F12 theory approximates the all-electron CCSD(T) basis-set-limit energy, it is of interest to estimate whether the contributions from post-CCSD(T) excitations are likely to be significant for the neutral, cation, and radical carboranes considered in this work. The percentage of the total atomization energy accounted for by the quasiperturbative triple excitations, %TAE[(T)],[20,64,65,66] has been shown to be a reliable energy-based diagnostic for the importance of post-CCSD(T) contributions to the total atomization energies. It has been shown that %TAE[(T)] $\leq$ 5% indicates that post-CCSD(T) contributions should not exceed ~0.5 kcal mol^{-1}, whilst %TAE[(T)] $\leq$ 10% indicates that post-CCSD(T) contributions should not exceed ~1.0 kcal mol^{-1}.[20] Table S1 of the Supporting Information gathers the %TAE[(T)] values for the $C_2B_{10}H_{12}$ isomers, their $C_2B_{10}H_{12}^+$ cations, and the 12 possible $C_2B_{10}H_{11}\bullet$ radical isomers. The %TAE$_e$[(T)] values for these species lie in a very narrow range of 1.9–2.2%. These values suggest that all the considered species are dominated by dynamical correlation effects, and that post-CCSD(T) contributions to the total atomization energies should be well below the 0.5 kcal mol^{-1} mark.

The above %TAE[(T)] diagnostics have been obtained from CCSD(T)/CBS values from W1-F12 theory. It is of interest to compare these %TAE[(T)] values to those obtained with much smaller double-ζ-type basis sets. %TAE[(T)] diagnostics obtained from with the 6-31G(d) basis sets are given in Table S1 of the Supporting Information. The %TAE[(T)] values obtained with the small 6-31G(d) basis set provide a useful approximation to the %TAE[(T)] values obtained at the CBS limit at a fraction of the computational cost. In particular, they are systematically lower than the CBS values by about 0.4%. This fairly weak basis-set dependence of the %TAE[(T)] diagnostic is in agreement with previous results which were obtained for a large dataset of much smaller systems.[20,21]

3.2. W1-F12 heats of formation for the $C_2B_{10}H_{12}$ carborane isomers. We begin by calculating the heats of formation for the three carborane isomers. Table 1 gives the component breakdown of the W1-F12 atomization energies as well as the final heats of formation at 0 K ($\Delta_f H^o_0$) and 298 K ($\Delta_f H^o_{298}$). The magnitude of the HF component (ΔHF) can be very large, ranging from 1922.71 (ortho-carborane) to 1942.92 (para-carborane) kcal mol^{-1}. These results are expected to be very close to the basis-set limit results. For example, we have recently shown that for the hydrocarbon cages (tetrahedrane, triprismane, and cubane) the ΔHF component from W1-F12 theory is less than 0.1 kcal mol^{-1} away from results obtained at the HF/VQZ-F12 level of theory.[67]

Table 1. Component breakdown of the W1-F12 atomization energies for the three carborane isomers and predicted theoretical enthalpies of formation (kcal mol^{-1}).

Component	Para	Meta	Ortho
ΔHF^a	1942.92	1940.63	1922.71
$\Delta CCSD\text{-}F12^a$	453.85	453.48	454.67
$\Delta(T)^b$	47.08	46.98	47.58
ΔCV^c	19.11	19.07	18.91
ΔRel^d	−1.31	−1.31	−1.30
ΔSO^e	−0.46	−0.46	−0.46
$\Delta DBOC^f$	0.39	0.38	0.38
$TAE_e{}^g$	2461.57	2458.77	2442.49
$\Delta ZPVE^h$	110.52	110.39	110.02
$TAE_0{}^i$	2351.05	2348.38	2332.47
$\Delta_f H°_0{}^j$	−40.41	−37.73	−21.83
$\Delta_f H°_{298}{}^k$	−50.63	−47.94	−31.97

[a]Extrapolated from the cc-pVDZ-F12 and cc-pVTZ-F12 basis sets. [b]Extrapolated from the aug'-cc-pVDZ and aug'-cc-pVTZ basis sets. [c]CCSD(T) core–valence correction obtained as: CCSD/cc-pwCVTZ + (T)/cc-pwCVTZ(no f). [d]CCSD(T)/cc-pVDZ-DK scalar relativistic correction. [e]First-order atomic spin-orbit correction. [f]HF/cc-pVTZ diagonal Born–Oppenheimer correction. [g]Vibrationless, relativistic, all-electron CCSD(T)/CBS total atomization energies. [h]ZPVE correction from B3LYP-D3/Def2-TZVPP harmonic frequencies (scaled by 0.99, see also ref. 27). [i]ZPVE-inclusive, relativistic, all-electron CCSD(T)/CBS total atomization energies. [j]CCSD(T)/CBS heats of formation at 0 K obtained using the following atomic heats of formation at 0 K: $\Delta_f H°_0$(H) = 51.633±0.000 (ATcT), $\Delta_f H°_0$(C) = 170.024±0.014 (ATcT), and $\Delta_f H°_0$(B) = 135.1 (ref. 68) kcal mol^{-1}.[69,70,71] [k]CCSD(T)/CBS heats of formation at 298 K obtained using enthalpy functions, H_{298}–H_0, from CODATA[72] for the elemental reference states and molecular enthalpy functions are obtained within the rigid rotor-harmonic oscillator approximation from B3LYP-D3/Def2-TZVPP harmonic frequencies.

The valence CCSD correlation contribution ($\Delta CCSD\text{-}F12$) increases the TAEs by amounts ranging from 453.48 (meta-carborane) to 454.67 (ortho-carborane) kcal mol^{-1}. We note, however, that for systems of this size these values can overestimate the CCSD/CBS values by chemically significant amounts. For example, extrapolating the CCSD-F12 energy from the V{D,T}Z-F12 basis set pair (with an extrapolation exponent of 3.67) overshoots the CCSD-F12/V{T,Q}Z-F12 values from W2-F12 theory by 0.13 (tetrahedrane), 0.33 (triprismane), and 0.52 (cubane) kcal mol^{-1}.[67] We expect that the deviations for the carboranes would be even larger. The valence (T) correlation contributions (Δ(T), Table 1) can be quite hefty, ranging between 46.98 (meta-carborane) and 47.58 (ortho-carborane) kcal mol^{-1}. The core–valence (ΔCV) correlation contributions are also relatively large, ranging from 18.91

(ortho-carborane) to 19.11 (para-carborane) kcal mol^{-1}. The scalar relativistic (ΔRel) and first-order spin-orbit coupling (ΔSO) contributions both reduce the atomization energies for all three systems by 1.30 and 0.46 kcal mol^{-1}, respectively. The DBOC contributions at the HF/cc-pVTZ level of theory amount to 0.38 kcal mol^{-1} for the three isomers. We note, however, that for systems with many hydrogen atoms correlation contributions to the DBOC are expected to reduce the ΔDBOC contribution to the total atomization energy by up to ~50%.[20,27,67] For example, for the hydrocarbon cages, the CCSD correlation correction to the DBOCs reduces the DBOC contribution to the TAEs by 0.08 (tetrahedrane), 0.11 (triprismane), 0.15 (cubane), 0.18 (pentaprismane), 0.22 (octahedrane), and 0.36 (dodecahedrane) kcal mol^{-1}.[67]

Summing up the ΔHF, ΔCCSD-F12, Δ(T), ΔCV, ΔRel, ΔSO, ΔDBOC and ΔZPVE contributions to the TAEs (Table 1) we obtain our best TAEs at 0 K (TAE$_0$) of: 2351.05 (para-carborane), 2348.38 (meta-carborane), and 2332.47 (ortho-carborane) kcal mol^{-1}. We convert these TAEs to heats of formation at 0 K using ATcT atomic heats of formation at 0 K,[69,70,71] and a semi-experimental atomic heat of formation for boron obtained from highly accurate W4 calculations.[64,68] Our best $\Delta_f H^\circ_0$ values are: –40.41 (para-carborane), –37.73 (meta-carborane), and –21.83 (ortho-carborane) kcal mol^{-1}. Consequently, these $\Delta_f H^\circ_0$ values are converted to heats of formation at 298 K ($\Delta_f H^\circ_{298}$) using the CODATA[72] enthalpy functions (H$_{298}$–H$_0$) for the elemental reference states and the enthalpy functions for the carborane isomers are obtained (within the rigid-rotor harmonic oscillator approximation) from the B3LYP-D3/Def2-TZVPP geometries and harmonic frequencies. Our best W1-F12 $\Delta_f H^\circ_{298}$ values are: –50.63 (para-carborane), –47.94 (meta-carborane), and –31.97 (ortho-carborane) kcal mol^{-1}.

3.3. W1-F12 C$_2$B$_{10}$H$_{12}$ isomerization energies. It is of interest to examine the W1-F12 components for the energies of meta- and ortho-carborane relative to the most stable para isomer. These results are gathered in Table 2. At the bottom-of-the-well the para isomer is more stable than the meta and ortho isomers by: 2.81 and 19.08 kcal mol^{-1}, respectively. We note that the scalar relativistic and DBOC contributions to the isomerization energies are practically nil, and the sum of the core-valence and valence (T) contributions amounts to less than 0.3 kcal mol^{-1}. Thus, fairly good estimations of the isomerization energies can be obtained at the clamped-nuclei, nonrelativistic, valence, CCSD/CBS level (Table 2).

Table 2. Component breakdown of the W1-F12 relative energies of meta-carborane and ortho-carborane (energies are given relative to para-carborane in kcal mol^{-1}).

Component[a]	Meta	Ortho
ΔHF	2.29	20.21
ΔCCSD-F12	0.37	−0.82
Δ(T)	0.10	−0.50
ΔCV	0.04	0.20
ΔRel	0.00	−0.01
ΔDBOC	0.00	0.01
E_e	2.81	19.08
ΔH^o_0	2.67	18.58
ΔH^o_{298}	2.69	18.65

[a]See footnotes *a–d, f, g, j,* and *k* to Table 1.

According to our W1-F12 isomerization energies at 0 K, the meta isomer is less stable than the para isomer by 2.67 kcal mol^{-1}, whilst the ortho isomer is less stable than the para isomer by 18.58 kcal mol^{-1}. These isomereization energies are consistent with the fact that the ortho isomer is the kinetic product from the addition of acetylenes to decarborane precursors. Upon heating to 425 °C the ortho isomer rearranges to the more stable meta isomer. Upon further heating to 600 °C the more thermally stable para isomer is obtained.[1]

Our W1-F12 isomerization energies differ slightly from previous theoretical values calculated at lower levels of theory. Specifically, the W1-F12 relative energies for meta- and ortho-carborane are lower by 0.9 and 0.5 kcal mol^{-1} from the value obtained by SN nearly two decades ago at the MP2/6-31G(d) level of theory.[16] For the energy of ortho-carborane relative to meta-carborane we obtain ΔH^o_0 = 15.91 kcal mol^{-1}, which deviates from the MP2/6-31G(d) value by only 0.3 kcal mol^{-1}. This ΔH^o_0 value is also in close agreement with the MP2/6-311+G(d,2p) value of 16.0 kcal mol^{-1} calculated by Knyazev *et al.*[17]

3.4. First ionization potentials. Table 3 gathers the component breakdown of the W1-F12 ionization potential. The ΔHF and valence ΔCCSD-F12 components account for the lion's share of the IPs. The Δ(T) component reduces the IPs by fairly modest amounts of 0.07 and 0.20 kcal mol^{-1} for the meta and

ortho isomers, respectively. However, for the para isomer the Δ(T) component reduces the IP by 0.85 kcal mol^{-1}. The core-valence component increases the IPs by chemically significant amounts ranging from 0.77 (meta-carborane) to 0.89 (para-carborane) kcal mol^{-1}. For all three isomers there is nearly perfect cancellation between the scalar relativistic and the DBOC corrections.

Table 3. Component breakdown of the W1-F12 first adiabatic ionization potentials for the carborane isomers (kcal mol^{-1}).

Component[a]	Para	Meta	Ortho
Δ**HF**	230.72	223.91	221.75
Δ**CCSD-F12**	14.97	17.06	17.63
Δ**(T)**	−0.85	−0.07	−0.20
Δ**CV**	0.89	0.77	0.78
Δ**Rel**	−0.05	−0.04	−0.04
Δ**DBOC**	0.05	0.04	0.07
TAE$_e$	245.73	241.68	239.99
$\Delta_f H°_0$	240.17	237.69	235.47
$\Delta_f H°_{298}$	241.50	238.45	236.54
Expt.[b]	237.5±4.6[73]	232.9±4.6[73]	232.9±4.6[73]
	244.4[74]	233.8[75]	233.6[75]

[a]See footnotes *a*–*d*, *f*, *g*, *j*, and *k* to Table 1. [b]The experimental values are taken from the NIST Webbook.[76]

The ionization potentials of the three carborane isomers have been determined experimentally,[73,74,75] and adopted by the NIST Chemistry WebBook as: 237.5±4.6 (para-carborane), 232.9±4.6 (meta- and ortho-carborane) kcal mol^{-1}. Our best theoretical values at 298 K are: 241.50±1 (para-carborane), 238.45±1 (meta-carborane), and 236.54±1 (ortho-carborane) kcal mol^{-1}. Assigning a conservative error bar of 1 kcal mol^{-1} to our W1-F12 values, to account for potential issues with basis-set incompleteness, electron correlation, and scaled harmonic ZPVE,[19] the discrepancy between theory and experiment is just below the sum of the respective uncertainties. The theoretical values suggest that the experimental IPs likely represent underestimations, namely they are lower than the theoretical ones by 4.00 (para-carborane), 5.55 (meta-carborane), and 3.64 (ortho-carborane) kcal mol^{-1}. In this context we note that it has been previously found that the older version of W1-F12 theory (i.e., W1 theory,[26]

which shows very similar performance to W1-F12 theory for first-row systems)[19] gives excellent performance for ionization potentials. For example for the 39 ionization potentials for the atoms and small molecules in the G2-1 ion test set, W1 theory attains an RMSD of 0.51 kcal mol^{-1} and a mean-absolute deviation (MAD) of 0.34 kcal mol^{-1}.[77]

Finally, it is worth pointing out that both W1-F12 theory and experiment predict that the IP for the para isomer is larger than the IPs for the meta and ortho isomers. However, whilst the experimental IPs for the meta and ortho isomers are practically identical, the theoretical IP for the meta isomer is higher by 1.91 kcal mol^{-1} than that for the ortho isomer. The increase in the theoretical IPs in the order para > meta > ortho is consistent with the observation that the electron withdrawing strength of the icosahedral carborane isomers increases in the order ortho > meta > para.[17,78]

3.5. C–H bond dissociation energies. Due to their high symmetries the carborane isomers have only one C–H BDE each. The component breakdown of the W1-F12 C–H BDEs is given in Table 4. The ΔHF and valence ΔCCSD-F12 components account for the lion's share of the BDEs. The sum of the Δ(T) and ΔCV components increases the BDEs by amounts ranging from 0.37 (ortho-carborane) to 0.62 (para-carborane) kcal mol^{-1}. The scalar relativistic and DBOC contributions are practically nil.

Table 4. Component breakdown of the W1-F12 C–H bond dissociation energies for the carborane isomers (kcal mol^{-1}).

Component[a]	Para	Meta	Ortho
ΔHF	95.81	96.90	97.19
ΔCCSD-F12	21.35	21.21	20.86
Δ(T)	0.30	0.23	0.04
ΔCV	0.32	0.31	0.33
ΔRel	−0.03	−0.03	−0.03
ΔDBOC	0.03	0.03	0.03
TAE$_e$	117.78	118.65	118.42
$\Delta_f H^o_0$	109.28	110.16	109.79
$\Delta_f H^o_{298}$	110.82	111.70	111.35

[a]See footnotes *a–d*, *f*, *g*, *j*, and *k* to Table 1.

The W1-F12 C–H BDEs at 298 K are: 110.82 (para-carborane), 111.70 (meta-carborane), and 111.35 (ortho-carborane) kcal mol^{-1}. Thus, the C–H bond strengths increase in the order: para-carborane < ortho-carborane < meta-carborane. We note that the BDEs reported by Serrano-Andrés *et al.*, which were calculated at the B3LYP/6-31G(d) level of theory, predict a different order, namely: ortho-carborane (108.1) < para-carborane (108.5) < meta-carborane (109.2 kcal mol^{-1}).[18] However, since the C–H BDEs spread over a relatively narrow range of only 0.88 kcal mol^{-1}, it is perhaps not surprising the B3LYP functional cannot predict the correct relative order of the BDEs.

3.6. B–H bond dissociation energies. Whilst the para-carborane has only one unique B–H BDE due to its D_{5h} symmetry, the ortho and meta isomers have four unique B–H BDEs each. Table 5 gives the component breakdown of the W1-F12 B–H BDEs. Inspection of Table 5 reveals that the W1-F12 components have similar magnitudes across the set of nine B–H BDEs. The ΔHF component ranges between 90.16 and 92.17, the ΔCCSD-F12 component ranges between 20.30 and 20.77, the Δ(T) component ranges between 0.24 and 0.33, and the ΔCV component ranges between 0.31 and 0.34 kcal mol^{-1}. The ΔRel and ΔDBOC components of the BDEs are practically nil.

Table 5. Component breakdown of the W1-F12 B–H bond dissociation energies for the carborane isomers (kcal mol^{-1}).

Component[a]	Para	Meta[b]				Ortho[b]			
	B–H	B_2–H	B_4–H	B_5–H	B_9–H	B_3–H	B_4–H	B_8–H	B_9–H
ΔHF	91.31	92.01	91.22	91.02	90.39	92.17	91.14	90.37	90.16
ΔCCSD-F12	20.59	20.66	20.57	20.58	20.35	20.77	20.42	20.30	20.30
Δ(T)	0.30	0.24	0.29	0.30	0.32	0.24	0.26	0.31	0.33
ΔCV	0.33	0.34	0.33	0.33	0.32	0.34	0.33	0.31	0.31
ΔRel	0.00	–0.01	0.00	0.00	0.00	–0.01	-0.01	0.00	0.00
ΔDBOC	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
TAE$_e$	112.53	113.26	112.41	112.24	111.39	113.53	112.15	111.30	111.10
$\Delta_f H^o_0$	105.68	106.40	105.61	105.42	104.65	106.68	105.31	104.55	104.38
$\Delta_f H^o_{298}$	107.13	107.85	107.06	106.87	106.10	108.13	106.77	106.00	105.82

[a]See footnotes *a–d, f, g, j*, and *k* to Table 1. [b]B_x–H indicates which B–H bond is being broken, x = 2, 4, 5, 9 (meta-carborane) and 3, 4, 8, 9 (ortho-carborane) (see Figure 1).

Overall the B–H BDEs spread over a wider range (of 2.31 kcal mol^{-1}) than the C–H BDEs (0.88 kcal mol^{-1}, *vide supra*). The weakest B–H bond (105.82 kcal mol^{-1}) is obtained for the B_9 position of ortho-carborane, whilst the strongest B–H bond (108.13 kcal mol^{-1}) is obtained for the B_3 position of ortho-carborane. As noted by Serrano-Andrés *et al*.[18] for the meta and ortho isomers, from B3LYP/6-31G(d) calculations, the strongest B–H bonds are obtained for the boron atoms closer to the carbon atoms. This observation is confirmed here at a much higher level of theory. For the meta isomer we obtain BDEs of 107.85 for the B_2 position which is bonded to both carbons; 107.06 for the B_4 position which is bonded to one carbon and is two bonds away from the other carbon; 106.87 for the B_5 position which is bonded to one carbon and is three bonds away from the other carbon; and 106.10 kcal mol^{-1} for the B_9 position which is not bonded to either carbon. For the ortho isomer we obtain BDEs of 108.13 for the B_3 position which is bonded to both carbons; 106.77 for the B_4 position which is bonded to one carbon and is two bonds away from the other carbon; 106.00 for the B_8 position which is two bonds away from both carbons; and 105.82 kcal mol^{-1} for the B_9 position which is two bonds away from one carbon and three bonds away from the other carbon.

The results provided in Tables 4 and 5 show that the B-centered radicals are more stable than the C-centered radicals. For example, at 0 K the B-centered radicals are more stable than the C-centered radicals by 3.60 (para isomer), 3.76–5.51 (meta isomer), and 3.11–5.41 (ortho isomer) kcal mol^{-1}. This observation can be explained in terms of the lower electronegativity of boron compared to carbon (2.0 vs 2.5).

3.7. Evaluation of the performance of lower-level composite ab initio procedures. The W1-F12 calculations carried out in this study can be computationally very demanding, in particular for the systems with low (or no) symmetry. For example, the W1-F12 calculations for the $C_2B_{10}H_{11}$ isomers with C_1 symmetry ran for 4800 CPU hours on Intel Xeon E5-4650L cores (at 3.1 GHz). For comparison, the G4 calculations for the same systems ran for 70 CPU hours, whilst the G4(MP2) calculations ran for less than 12 CPU hours on the same cores. In addition, the W1-F12 calculations also place strenuous demands on the computational resources in terms of memory and disk, for example the abovementioned W1-F12 calculations ran on nodes with 512 GB of RAM, whilst the G4 and G4(MP2) calculations ran on nodes with 64 GB of RAM. It is therefore of interest to evaluate the performance of more economical composite ab initio procedures for their ability to accurately calculate the thermochemical properties reported in the previous sections. Table 6 gives an overview of the

performance of a number of Gn and CBS composite procedures for isomerization, ionization, and bond dissociation energies for the $C_2B_{10}H_{12}$ carborane isomers.

Table 6. Deviations and overall error statistics from W1-F12 values of isomerization, ionization, C–H bond dissociation, and B–H bond dissociation energies for carboranes obtained by Gn and CBS composite ab initio procedures (kcal mol^{-1}).

		G4	G3B3	G3	G4(MP2)	G4(MP2)-6X	G3(MP2)B3	G3(MP2)	CBS-QB3
Isomerization	meta	0.19	0.19	0.02	0.13	0.14	0.12	−0.04	[c]
	ortho	−0.07	−0.07	−0.05	−0.22	−0.15	−0.20	−0.17	[c]
Ionization	para	−1.24	0.68	1.07	−3.11	−0.55	0.50	0.71	[c]
	meta	−1.40	0.50	2.49	−3.23	−0.66	0.34	2.19	0.12
	ortho	−1.40	0.47	1.09	−3.19	−0.64	0.35	0.84	−1.01
C–H BDE	para	−2.53	0.08	0.50	−4.15	−1.56	−0.27	0.20	[c]
	meta	−2.55	0.10	0.51	−4.14	−1.56	−0.23	0.23	−0.24
	ortho	−2.65	−0.01	0.45	−4.26	−1.68	−0.37	0.14	−0.41
B–H BDE	para	−1.88	0.67	0.79	−3.70	−1.05	0.12	0.30	[c]
	meta B_2–H[a]	−2.39	0.22	0.74	−4.25	−1.58	−0.35	0.22	0.58
	meta B_4–H[a]	−2.32	0.30	0.74	−4.15	−1.49	−0.27	0.24	0.52
	meta B_5–H[a]	−2.32	0.28	0.75	−4.15	−1.49	−0.27	0.25	2.03
	meta B_9–H[a]	−2.33	0.28	0.78	−4.13	−1.49	−0.24	0.30	0.38
	ortho B_3–H[a]	−2.22	0.37	0.68	−4.08	−1.40	−0.20	0.16	2.28
	ortho B_4–H[a]	−2.21	0.37	0.76	−4.02	−1.37	−0.17	0.28	0.53
	ortho B_8–H[a]	−2.21	0.36	0.79	−4.00	−1.36	−0.17	0.32	0.41
	ortho B_9–H[a]	−2.25	0.38	0.77	−4.04	−1.40	−0.14	0.29	0.76
Error statistics[b]	RMSD	2.04	0.37	0.92	3.69	1.25	0.27	0.63	1.01
	MAD	1.89	0.31	0.76	3.47	1.15	0.25	0.41	0.54
	MSD	−1.87	0.30	0.76	−3.45	−1.13	−0.09	0.38	0.49
	LD	−2.65	0.68	2.49	−4.26	−1.68	0.50	2.19	2.28

[a]B_x–H indicates on which B–H bond is being broken (see Figure 1). [b]The error statistics are over all the chemical properties listed above; RMSD = root-mean-square deviation, MAD = mean-absolute deviation, MSD = mean-signed deviation, LD = largest deviation. [c]We were unable to obtain these values due to convergence issues with the MP2 step for the para-$C_2B_{10}H_{12}$ isomer.

All of the considered composite procedures give excellent performance for the isomerization energies of meta- and ortho-carborane relative to the para isomer. The deviations

from W1-F12 are smaller than 1 kJ mol^{-1} for all the considered procedures. In particular, G3 theory can be singled out as the best performing procedure with near-zero deviations.

The ionization energies for the para, meta, and ortho isomers represent a harder test for the Gn and CBS composite procedures. Of the G4, G3B3, and G3 procedures, which have a similar computational cost, G3B3 shows the best performance with deviations ranging between 0.47 (ortho-carborane) and 0.68 (para-carborane) kcal mol^{-1}. The G3 and G4 procedures result in deviations (in absolute value) above the 1 kcal mol^{-1} mark for all the isomers. However, the G3 procedure systematically overestimates the W1-F12 ionization energies, whilst G4 systematically underestimates them. Of the computationally more economical Gn(MP2)-type procedures G4(MP2) shows particularly poor performance with deviations of over 3 kcal mol^{-1} (all underestimations) for all three isomers. G4(MP2)-6X represents a significant improvement over G4(MP2), with deviations (underestimations) ranging between 0.55 and 0.66 kcal mol^{-1}. The G3(MP2)B3 procedure shows the best performance with deviations (all overestimations) ranging between 0.34 and 0.50 kcal mol^{-1}.

The C–H and B–H BDEs represent an even harder test for most of the composite procedures. In particular, the G4-type procedures result in poor performance with deviations ~4 kcal mol^{-1} (G4(MP2)), ~2 kcal mol^{-1} (G4), and ~1.5 kcal mol^{-1} (G4(MP2)-6X). On the other hand, G3(MP2)B3 and G3(MP2) show exceptionally good performance with all deviations (in absolute value) below the 0.4 kcal mol^{-1} mark.

Overall, we obtain the following RMSDs for the isomerization, ionization, and bond dissociation energies: 3.69 (G4(MP2)), 2.04 (G4), 1.25 (G4(MP2)-6X), 1.01 (CBS-QB3), 0.92 (G3), 0.63 (G3(MP2)), 0.37 (G3B3), and 0.27 (G3(MP2)B3) kcal mol^{-1}. Thus, we recommend the G3(MP2)B3 procedure due to its superb performance-to-computational cost ratio.

A question that naturally arises is why do the G3 and G3B3 procedures perform better than the more recent G4 procedures? Let us start by comparing the performance of the G3-type procedures with that of the G3B3-type procedures. The G3B3 and G3(MP2)B3 procedures (RMSD = 0.37 and 0.27 kcal mol^{-1}, respectively) outperform the G3 and G3(MP2) procedures (RMSD = 0.92 and 0.63 kcal mol^{-1}, respectively). In part, the better performance of the G3B3-type procedures may be attributed to the better reference geometries and ZPVEs used. Namely, the G3B3-type procedures use geometries and ZPVEs calculated at the B3LYP/6-31G(d) level of theory, whilst the G3-type procedures use MP2/6-31G(d) geometries and HF/6-31G(d) ZPVEs.[52]

These results indicate that the significant difference in performance between the G3-type and G4-type procedures cannot be solely attributed to the different reference geometries and ZPVEs used in these procedures. Another difference between the G3- and G4-type procedures is the highest correlation level used for calculating the base energy, i.e., QCISD(T)/6-31G(d) in the G3-type procedures and CCSD(T)/6-31G(d) in the G4-type procedures. However, for all the thermochemical properties considered these two levels of theory provide very similar performance. With the exception of the IPs, the differences between these two levels of theory are below 0.2 kcal mol^{-1}. For the IPs the differences can reach up to 0.4 kcal mol^{-1} (see Table S2 of the Supporting Information). Another key difference between the G3- and G4-type procedures is the E(HF/limit) correction term which is used in G4 and G4(MP2), but neglected in the G3-type procedures.[52] Inspection of Table S2, however, reveals that this correction cannot account for the large difference in performance between the G3- and G4-type procedures for the BDEs.

Based on the results of the preceding paragraph, the difference in performance between the G3- and G4-type procedures is mainly attributed to the different higher-level correction terms E(HLC) that are used in the G3- and G4-type procedures. This is consistent with the fact that the performance of the G3- and G4-type procedures is similar for the isomerization energies, which involve only closed-shell species (i.e., for which E(HLC) = 0). For the thermochemical properties which involve open-shell systems (i.e., IPs and BDEs) the E(HLC) correction terms are quite different between the G3- and G4-type procedures and therefore their performance varies significantly. Table S3 of the Supporting Information compares between the E(HLC) term in G3(MP2) and G4(MP2). As can be seen in G3(MP2) the E(HLC) term systematically increases the IPs and BDEs, whilst in G4(MP2) the E(HLC) term systematically decreases them. Furthermore, the differences between the E(HLC) terms are similar to the overall differences between G3(MP2) and G4(MP2) for the IPs and BDEs. To this end we note that G4(MP2)-6X procedure which employs six additional empirical scaling factors in order to improve the performance for general thermochemistry[21,58,79] performs significantly better than G4(MP2) and even G4, nevertheless, it is still outperformed by the G3-type procedures.

4. Conclusions

We obtain the heats of formation, isomerization energies, ionization potentials, and C–H and B–H bond dissociation energies for the carborane isomers using the high-level ab initio W1-

F12 thermochemical protocol. To the best of our knowledge the thermochemical properties of the carboranes have not been previously studied at the CCSD(T)/CBS level of theory. Thus, this investigation provides the most accurate thermochemical values that are presently available for these compounds.

Our best W1-F12 heats of formation ($\Delta_f H^{\circ}_{298}$) values are: −50.63 (para-carborane), −47.94 (meta-carborane), and −31.97 (ortho-carborane) kcal mol^{-1}. According to these W1-F12 values the meta isomer is less stable than the para isomer by 2.69 kcal mol^{-1}, whilst the ortho isomer is less stable than the para isomer by 18.65 kcal mol^{-1} (Table 2). These isomereization energies are in reasonably good agreement with previous theoretical values obtained at much lower levels of theory.

Our W1-F12 ionization potentials at 298 K are: 241.50 (para-carborane), 238.45 (meta-carborane), and 236.54 (ortho-carborane) kcal mol^{-1}. These values agree with the experimental values adopted by the NIST Chemistry WebBook to within overlapping uncertainties, however they suggest that the experimental IPs represent underestimations. Namely, they are lower than the W1-F12 values by amounts of 4.00 (para-carborane), 5.55 (meta-carborane), and 3.64 (ortho-carborane) kcal mol^{-1}.

The W1-F12 C–H BDEs spread over a narrow range of 0.88 kcal mol^{-1}, specifically the BDEs at 298 K are: 110.82 (para-carborane), 111.70 (meta-carborane), and 111.35 (ortho-carborane) kcal mol^{-1}. The B–H BDEs spread over a wider range (of 2.31 kcal mol^{-1}), where the strongest B–H bonds are obtained for the boron atoms closer to the carbon atoms.

Finally, we evaluate the performance of a range of lower-cost Gn and CBS composite ab initio procedures. We find that the G3(MP2)B3 procedure offers a stellar price-performance ratio with an overall RMSD of only 0.27 kcal mol^{-1} for the isomerization, ionization, and bond dissociation energies. However, the more recent G4-type procedures provide relatively poor performance with RMSDs of 3.69 (G4(MP2)), 2.04 (G4), and 1.25 (G4(MP2)-6X) kcal mol^{-1}.

Supplementary data

Diagnostics indicating the importance of post-CCSD(T) correlation effects for the species considered in this work (Table S1); Deviations and error statistics for some energetic components used in the Gn methods (Table S2); Higher-level corrections used in the G3(MP2) and G4(MP2) methods (Table S3); B3LYP-D3/Def2-TZVPP optimized geometries for the

species considered in this work (Table S4); and full references for ref. 22 (Molpro 2012.1), ref. 41 (CFOUR), and ref. 51 (Gaussian 09) (Table S3).

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