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REGULAR ARTICLE

Gas-phase enthalpies of formation, acidities, and strain energies of the [*m*, *n*]polyprismanes ($m \geq 2$; $n = 3$–8; $m \times n \leq 16$): a CBS-Q//B3, G4MP2, and G4 theoretical study

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Abstract Gas-phase standard state (298.15 K, 1 atm) enthalpies of formation ($\Delta_f H^o_{(g)}$) and enthalpies ($\Delta_{acid} H^o_{(g)}$) and free energies ($\Delta_{acid} G^o_{(g)}$) of acid dissociation were calculated for the [*m*, *n*]polyprismanes ($m \geq 2$; $n = 3$–8; $m \times n \leq 16$) using the composite method CBS-Q//B3, G4MP2, and G4 levels of theory. Excellent agreement was obtained between the theoretical estimates and experimental values for [2, 4]polyprismane (cubane), the only member with reliable experimental data. Gas-phase acidities of the [2, 3], [2, 4], and [2, 5]polyprismanes correlate well with percent s-character of the C–H bonds as determined by nuclear magnetic resonance spectroscopy. Based on this correlation, and calculations on the [2, *n*] ($n = 3$–8) series, no substantial change in the gas-phase acidity or C–H bond s-character is expected with increasing [2,*n*] polyprismane ring size at $n = 6$–8. Where three or more stacked [*m*, *n*]polyprismane rings are present ($m > 2$), geometry optimizations for the deprotonated anions converged on cage-opened non-prismatic geometries, suggesting these compounds may be structurally unstable to gas-phase deprotonation/protonation cycles and potentially preventing reliable experimental measurement or calculation of their acidities. Total strain energies (E_{str}) increase with larger [*m*, *n*]polyprismane size, and strain energies per one C–C bond (E^{CC}_{str}) increase with increasing stack height within a given ring size series. Within a given stack height, E^{CC}_{str} reaches a minimum with a ring size of five, increasing with either decreasing or increasing ring size away from this minima. E_{str} and E^{CC}_{str} do not correlate with gas-phase acidity, likely because the deprotonated anionic [2, *n*]polyprismane geometry retains approximately equal strain as the undissociated species despite substantial geometry changes due to carbon acid dissociation.

Keywords Polyprismanes · Enthalpy of formation · Gas-phase acidity · Strain energy · Composite methods

1 Introduction

Cage-type polyhedral hydrocarbons have attracted substantial attention because of their non-classical carbon bonding, unusual ring strain, σ-aromaticity/antiaromaticity, range of possible isomerization reactions, and unique physicochemical properties [1–12]. A subset of these general structures, the [*m*, *n*]polyprismanes are of particular interest due to the presence of semiplanar carbon centers, applications in nanoengineered structures, and use as potential high energy density materials (HEDMs) and energy storage systems [4, 8, 13–16]. To help provide a common terminology for the field, Lewars [7] has developed a [*m*,*n*]polyprismane numbering system whereby '*m*' denotes the number of stacked rings and '*n*' is the carbon size of each stacked ring. Only the [2, 3] (prismane), [2, 4] (cubane), and [2, 5] (pentaprismane) members have been synthesized [17–19]; the remainder remain high priority synthetic targets whose thermodynamic properties are of substantial significance.

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In the current work, we report the results of Complete Basis Set (CBS) and Gaussian-4 (G4) method calculations on the gas-phase enthalpies of formation, acidities, and strain energies for the [*m*, *n*]polyprismanes ($m \geq 2$; $n = 3$–8; $m \times n \leq 16$). Because of the interest in using these compounds as HEDMs and in nanostructures, high level theoretical estimates are needed to better constrain the thermochemical properties of widely studied members, and to also help assess the accuracy of lower cost density functional theory (DFT) approaches likely to be employed for future studies of larger [*m*, *n*]polyprismanes. The physicochemical properties of the [*m*, *n*]polyprismanes are also of fundamental value, given the widespread interest in studies of highly strained organic compounds that probe the limits of our understanding regarding structure and bonding.

2 Computational methods

Calculations were conducted with Gaussian 09 [20] and the CBS-Q//B3 [21, 22], G4MP2 [23], and G4 [24] composite methods using gas-phase starting geometries obtained with the PM6 semiempirical method [25] as implemented in MOPAC 2009 (http://www.openmopac.net/; v. 9.281). Molecular enthalpies and free energies include zero point and thermal corrections. Only the lowest energy conformation of each molecule was considered. Optimized structures were confirmed as true minima by vibrational analysis at the same level. G09 archive entries are provided in the Supplementary Materials with optimized geometries and energies at each stage of the CBS-Q//B3, G4MP2, and G4 calculation processes. All compounds have D_{nh} prismatic symmetry with no imaginary frequencies.

3 Results and discussion

Gas-phase standard state (298.15 K, 1 atm) enthalpies of formation ($\Delta_f H^o_{(g)}$) for the [*m*, *n*]polyprismanes ($m \geq 2$; $n = 3$–8; $m \times n \leq 16$; Fig. 1) are given in Table 1. Geometrical parameters do not vary significantly with level of theory (bond lengths within $\sim\pm 0.001$–0.002 Å, bond angles within $\sim\pm 0.1$–$0.2°$), and are in agreement with previous theoretical and experimental reports [7, 13–18, 26–44] (Fig. 1). $\Delta_f H^o_{(g)}$ values were calculated for all compounds using the atomization enthalpy approach [45, 46]. Selected homodesmic and isodesmic approaches were also used for applicable compounds. Due to computational expense, G4MP2 calculations were not completed for the [2, 8]polyprismane, and G4 calculations were only completed on the [2, 3], [2, 4], and [3, 3]polyprismanes. An experimental $\Delta_f H^o_{(g)}$ of 148.7 ± 1.0 kcal/mol is available for the [2, 4]polyprismane (cubane) [47]; our CBS-Q//B3 (148.9 kcal/mol), G4MP2 (144.2 kcal/mol), and G4 (145.2 kcal/mol) atomization-based estimates are in good agreement.

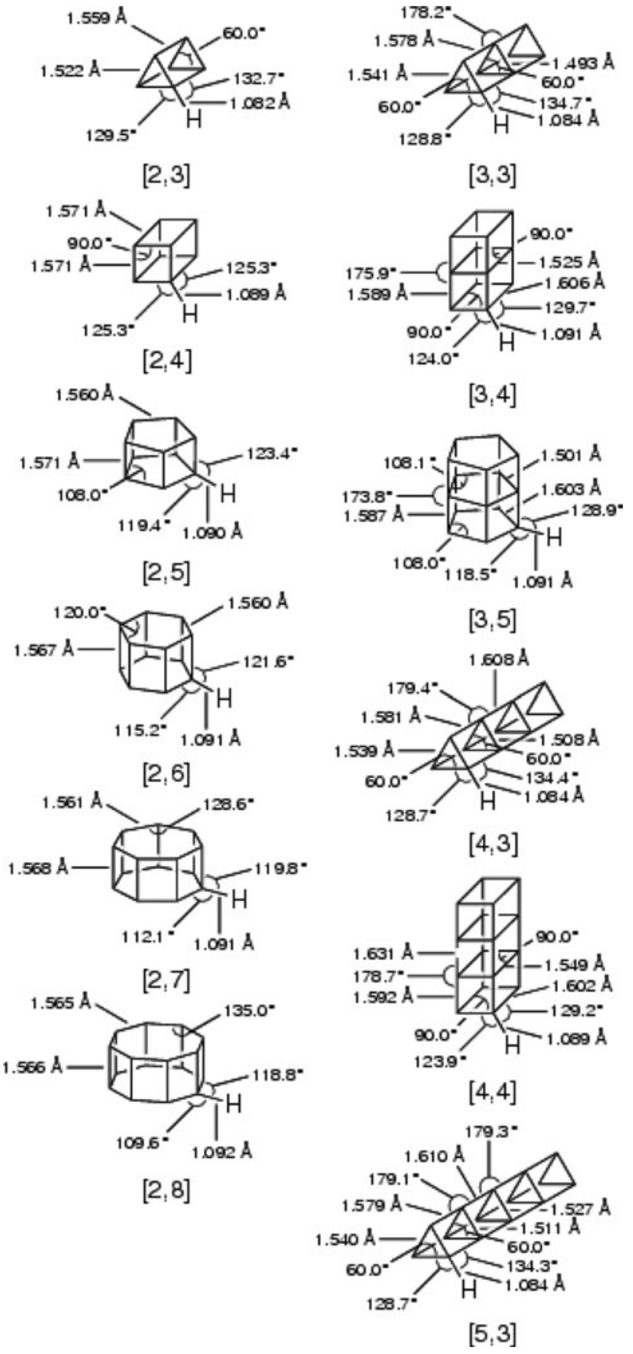

Fig. 1 Structures with gas-phase standard state (298.15 K, 1 atm) CBS-Q//B3 optimized bond lengths and angles for the [*m*, *n*]polyprismanes ($m \geq 2$; $n = 3$–8; $m \times n \leq 16$)

We note that the experimental $\Delta_f H^o_{(g)}$ for cubane has been called into question based on sublimation data [48, 49] that conflicts with the historical estimate, as well as justified critiques (i.e., concerns over subjective corrections for unburned residues in the original measurements)

Table 1 Gas-phase standard state (298.15 K, 1 atm) enthalpies of formation ($\Delta_f H^o_{(g)}$) for the [m, n]polyprismanes ($m \geq 2$; $m \times n \leq 16$) at the CBS-Q//B3, G4MP2, and G4 levels of theory

	Current work	Literature
[2, 3]	$136.1_{\text{CBS-Q//B3}}$, 132.2_{G4MP2}, 133.2_{G4}	136.7_{MMP2A} [77], 121.9_{MNDO} [77, 78], 165.0_{AM1} [26, 77], 136.0_{PM3} [77], $136.4/136.2_{\text{SCF/6-31G*(RMP2)}}$ [26], $136.8 \pm 5.8_{\text{(HF,MP2,B3LYP)/6-31G*}}$ [29], $130.7/129.9_{\text{G2(MP2,SVP)}}$ [79], $137.1/131.4_{\text{G2(MP2)}}$ [79, 80], $133.0_{\text{G2(MP2)}}$ [28], $137.8/131.9_{\text{G2(MP3)}}$ [79], $136.2/130.7_{\text{G2}}$ [79],53], $135.3/131.3_{\text{CBS-Q}}$ [79], $132.3/134.3_{\text{CBS-APNO}}$ [79], $135.0/134.0/135.1_{\text{G3(B3LYP)}}$ [81, 82], $134.6/133.8_{\text{G3(MP2)}}$ [80], $135.7/133.8_{\text{G3}}$ [80]
[2, 4]	$148.9_{\text{CBS-Q//B3}}$, 144.2_{G4MP2}, 145.2_{G4}	$148.7 \pm 1.0_{\text{expt}}$ [47], 148.8_{MM2} [78], 148.9_{MM2} [37], 99.1_{MNDO} [12 [26], 33], 151.2_{AM1} [26], 151.1_{AM1} [13], 113.8_{PM3} [13], $149.9_{\text{HF/STO-3G}}$ [83], $137.9_{\text{HF/4-31G}}$ [83], $139.8_{\text{HF/6-31G*}}$ [83], $145.1_{\text{SCF/3-21G}}$ [37], $147.1_{\text{SCF/6-31G*}}$ [37], $148.5/146.3_{\text{SCF/6-31G*(RMP2)}}$ [84], $171.1_{\text{RHF/6-31G*}}$ [14], $170.8_{\text{SVWN/6-31G*}}$ [27], $124.3_{\text{BP/6-31G*}}$ [27], $114.8_{\text{BLYP/6-31G*}}$ [27], $122.3_{\text{B3LYP/6-31G*}}$ [27], $108.5_{\text{BLYP/6-31+G**//BLYP/6-31G*}}$ [27], $128.6_{\text{B3LYP/6-31+G**//BLYP/6-31G*}}$ [27], $158.1_{\text{MP2/6-31G*//RHF/6-31G*}}$ [14], $149.1_{\text{MP2/6-31G(d)*//RHF/6-31G(d)*}}$ [16], $142.7 \pm 0.9_{\text{(HF,MP2,B3LYP)/6-31G*}}$ [29], $146.0_{\text{G3(MP2)}}$ [85], $143.2_{\text{G2(MP2)}}$ [86], 142.3_{G2} [86], $145.1_{\text{G3//B3LYP}}$ [86], 145.5_{G3} [86], $146.5 \pm 2.3_{\text{G2(MP2),G2,G3//B3LYP,G3[avg],homodesmic}}$ [86], 159.0 ± 1.2^{b} [87], 158.5^{c} [87]
[2, 5]	$124.4_{\text{CBS-Q//B3}}$, 119.5_{G4MP2}	114.7_{MM2} [78], 72.2_{MNDO} [26], 117.7_{AM1} [26], $115.4_{\text{SCF/3-21G}}$ [37], $121.2/122.0_{\text{SCF/6-31G*}}$ [37], $119.6/120.5_{\text{SCF/6-31G*(RMP2)}}$ [37], $123.9 \pm 7.2_{\text{(HF,MP2,B3LYP)/6-31G*}}$ [29]
[2, 6]	$158.9_{\text{CBS-Q//B3}}$, 152.9_{G4MP2}	129.2_{MM2} [78], 80.4_{MNDO} [26], 139.9_{AM1} [26], $160.3_{\text{SCF/3-21G}}$ [37], $154.5/154.7_{\text{SCF/6-31G*}}$ [37], $153.1/153.6_{\text{SCF/6-31G*(RMP2)}}$ [37], $157.3 \pm 7.9_{\text{(HF,MP2,B3LYP)/6-31G*}}$ [29]
[2, 7]	$214.2_{\text{CBS-Q//B3}}$, 207.1_{G4MP2}	173.8_{MM2} [78], 116.4_{MNDO} [26], 191.0_{AM1} [26], $212.0_{\text{SCF/6-31G*(RMP2)}}$ [37], $215.5 \pm 7.7_{\text{(HF,MP2,B3LYP)/6-31G*}}$ [29]
[2, 8]	$279.3_{\text{CBS-Q//B3}}$	172.7_{MNDO} [78], 259.2_{AM1} [26], $283.1_{\text{SCF/6-31G*(RMP2)}}$ [26], $285.1 \pm 6.5_{\text{(HF,MP2,B3LYP)/6-31G*}}$ [29]
[3, 3]	$310.7_{\text{CBS-Q//B3}}$, 303.6_{G4MP2}, 306.1_{G4}	n/a[a]
[3, 4]	$383.2_{\text{CBS-Q//B3}}$, 373.9_{G4MP2}	n/a
[3, 5]	$385.9_{\text{CBS-Q//B3}}$, 375.4_{G4MP2}	n/a
[4, 3]	$478.1_{\text{CBS-Q//B3}}$, 467.7_{G4MP2}	n/a
[4, 4]	$598.1_{\text{CBS-Q//B3}}$, 583.9_{G4MP2}	n/a
[5, 3]	$643.1_{\text{CBS-Q//B3}}$, 629.5_{G4MP2}	n/a

Previous theoretical and experimental values reported in the literature are also provided. Subscripts indicate levels of theory or experimental values. Values are in kcal/mol

[a] Theoretical or experimental literature values not available

[b] Calculated using the constant enthalpy of formation differences between the hydrocarbon and its methyl ester during studies on 1,4-dimethylcubane dicarboxylate

[c] Calculated using the bicyclobutane strain energy difference between the hydrocarbon and its methyl ester during studies on 1,4-dimethylcubane dicarboxylate

regarding the quality of the solid state combustion data. Karpushenkava et al. [29] have recently proposed a revised experimental $\Delta_f H^o_{(g)}$ of 142.7 ± 1.0 kcal/mol for cubane based on the updated sublimation studies. Our G4 $\Delta_f H^o_{(g)}$ atomization-based estimate lies between these two competing $\Delta_f H^o_{(g)}$ values and cannot clearly discriminate as to which—if either—is correct. No other experimental $\Delta_f H^o_{(g)}$ values are available in the NIST database [50, 51] for these [m, n]polyprismanes.

For all compounds, the G4 and G4MP2 $\Delta_f H^o_{(g)}$ atomization-based estimates are lower than the corresponding CBS-Q//B3 atomization-based estimates by 4–14 kcal/mol, with the difference between the CBS-Q//B3 and G4/G4MP2 values increasing with increasing molecular size. We have previously shown that, in general, $\Delta_f H^o_{(g)}$ estimates using the atomization approach and CBS-Q//B3 method exhibit scaling errors with molecular size, whereas the G4/G4MP2 level methods display effective chemical accuracy without substantial scaling errors [52–54]. Thus, we expect the CBS-Q//B3 $\Delta_f H^o_{(g)}$ estimate of 279.3 kcal/mol for the [2, 8]polyprismane to be too high by about 14 kcal/mol; the true $\Delta_f H^o_{(g)}$ for the [2, 8]polyprismane is likely near 265 kcal/mol. A number of previous $\Delta_f H^o_{(g)}$ estimates have been reported for the [2, n]polyprismanes under consideration at various semiempirical, ab initio, density functional, and composite levels of theory, as provided in Table 1. While there is wide variation among different methods, we note that in some cases, selected historical estimates (often at much lower levels of theory, such as SCF/3-21G) are very close to the current G4/G4MP2 values.

Various isodesmic and homodesmic approaches have been applied to estimate the $\Delta_f H^o_{(g)}$ of [2, *n*]polyprismanes in the literature, particularly for the [2, 3] and [2, 4] members. Wang and Law [55] applied the following isodesmic reaction for $(CH)_n$ isomers (i.e., [2, *n*]polyprismanes):

$$[2, n]\text{polyprismane} + 4n\,CH_4 \rightarrow 3n\,C_2H_6$$

Karpushenkava et al. [29] proposed the following homodesmic reaction for $(CH)_n$ isomers:

$$[2, n]\text{polyprismane} + n/2\,\text{cyclohexane} \rightarrow n/2\,\text{adamantane}$$

Homodesmic reactions anchored to the experimental $\Delta_f H^o_{(g)}$ of cubane ([2, 4]polyprismane) can also be used to estimate $\Delta_f H^o_{(g)}$ of other [2, *n*]polyprismanes, yielding an equation with the following general stoichiometry:

$$(4/n)\,[2, n]\text{polyprismane} \rightarrow [2, 4]\text{polyprismane}$$

Application of these schemes toward the [2, *n*]polyprismanes ($n \leq 8$) using our CBS-Q//B3, G4MP2, and G4 data yields reasonable agreement with the atomization-based $\Delta_f H^o_{(g)}$ estimates (Table 2). However, isodesmic and homodesmic approaches have inherently lower $\Delta_f H^o_{(g)}$-precision than atomization methods due to the respective uncertainties of the underlying experimental data used in such calculations. The experimental $\Delta_f H^o_{(g)}$ for carbon (171.29 ± 0.11 kcal/mol [56]) and hydrogen (52.103 ± 0.001 kcal/mol [56]) atoms are much better constrained for the atomization method than are experimental $\Delta_f H^o_{(g)}$ for methane (range of $\Delta_f H^o_{(g)}$ from −17.5 ± 0.3 to −17.9 kcal/mol [57, 58, 59]), ethane (–20.0 ± 0.1 to −20.2 ± 0.1 kcal/mol [60, 61]), cyclohexane (–29.4 ± 0.2 to −29.8 kcal/mol [62, 63]), adamantane (−30.8 ± 1 to −33.2 kcal/mol[64, 65, 66]), and cubane (142.7 ± 1.0 to 148.7±1.0 kcal/mol [29], 47]) used in the isodesmic/homodesmic approaches.

This variability in the experimental database leads to inherent variability in the calculated $\Delta_f H^o_{(g)}$ from isodesmic and homodesmic schemes, particularly if amplified by stoichiometries greater than unity in the respective equations (e.g., a [2, 8]polyprismane $\Delta_f H^o_{(g)}$ isodesmic calculation employs stoichiometric coefficients of 32 methane and 24 ethane molecules per molecule of [2, 8]polyprismane). Choosing the input $\Delta_f H^o_{(g)}$ for isodesmic/homodesmic methods based on the best $\Delta_f H^o_{(g)}$ agreement for a member of the target compound set with an experimental data point is not a rigorous strategy, as the output experimental data being compared to for method calibration may itself be incorrect. Cubane offers an excellent case study in this regard, as it is the only [*m*, *n*]polyprismane with experimental $\Delta_f H^o_{(g)}$ data, but the estimates (neither of which can be readily discounted) differ by 6 kcal/mol. In addition, the available $\Delta_f H^o_{(g)}$ for methane, ethane, cyclohexane, and adamantane allow us to tune the G4 predicted $\Delta_f H^o_{(g)}$ for cubane from 135.9 to 144.3 kcal/mol with the isodesmic scheme and from 146.3 to 151.7 kcal/mol at the G4MP2 level with the homodesmic scheme.

In contrast, a single $\Delta_f H^o_{(g)}$ estimate arises for hydrocarbons from the atomization method using the atomic enthalpies for which a scientific consensus has been reached. The resulting $\Delta_f H^o_{(g)}$ is a value all researchers using a particular level of theory and compound should be able to reproduce (ignoring the 0.003 and 0.06% experimental errors in the $\Delta_f H^o_{(g)}$ for the hydrogen and carbon atoms, respectively). In an atomization approach error analysis, using the lower (C: 171.18 kcal/mol; H: 52.101 kcal/mol) and upper (C: 171.40 kcal/mol; H: 52.104 kcal/mol) bounds of the atomic experimental $\Delta_f H^o_{(g)}$ for carbon and hydrogen atoms varies the atomization enthalpy method $\Delta_f H^o_{(g)}$ estimate for cubane at the G4 level by <±0.9 kcal/mol, much less than the ±∼9 kcal/mol $\Delta_f H^o_{(g)}$ estimate tuning achievable using the isodesmic scheme and range of experimental $\Delta_f H^o_{(g)}$ for methane and ethane. For many isodesmic and homodesmic approaches in the literature, the underlying experimental $\Delta_f H^o_{(g)}$ being applied are often not provided nor is an effort made to conduct a corresponding sensitivity analysis that contextualizes the likely method precision. Although isodesmic and homodesmic approaches can offer potential insights into the thermochemistry of highly strained molecules, with the high variability in the target experimental $\Delta_f H^o_{(g)}$ database to which these methods may be calibrated, and the imprecision of the underlying $\Delta_f H^o_{(g)}$ values for non-target molecules used in the calculations, these methods are susceptible to a higher level of imprecision than atomization approaches.

The Benson group additivity rules for estimating $\Delta_f H^o_{(g)}$ have demonstrated success for a broad range of relatively unstrained organic compounds [67–70]. Application of this approach to the [*m*, *n*]polyprismanes only offers modest agreement with the CBS-Q//B3, G4MP2, and G4 atomization enthalpy results for cubane and pentaprismane ([2, 5]polyprismane) (Table 3). The disagreement between the methods increases with increasing ring size (*n*) and stack height (*m*), with discrepancies approaching 200 kcal/mol for the [5, 3]polyprismane. In general, the Benson additivity scheme underestimates $\Delta_f H^o_{(g)}$ for highly strained compounds such as the [*m*, *n*]polyprismanes because appropriate strain correction factors are not available. Our Benson approach $\Delta_f H^o_{(g)}$ of 141.6 kcal/mol for cubane is in excellent agreement with the previous Benson estimate of 142.0 kcal/mol by Hassenruck et al.

Table 2 Gas-phase standard state (298.15 K, 1 atm) enthalpies of formation ($\Delta_f H^o_{(g)}$) for the [m, n]polyprismanes ($m = 2$; $m \times n \leq 16$) at the CBS-Q//B3, G4MP2, and G4 levels of theory using isodesmic and homodesmic reaction schemes previously employed in the literature

	Isodesmic[a]			Homodesmic[b]		Homodesmic[c]		
	CBS-Q//B3	G4MP2	G4	CBS-Q//B3	G4MP2	CBS-Q//B3	G4MP2	G4
[2, 3]	133.0 [−3.1]	132.2 [−0.7]	133.2 [−2.0]	137.1 [1.0]	135.9 [3.7]	136.0 [−0.1][d]/131.5[e] [−4.6]	135.6[d] [3.4]/131.1[e] [−1.1]	135.8[d] [2.6]/131.3 [−1.9]
[2, 4]	144.7 [−4.2]	144.2 [−1.1]	145.2 [−2.7]	150.2 [1.3]	149.1 [4.9]	n/a[f]	n/a	n/a
[2, 5]	119.1 [−5.3]	119.5 [−1.3]	n/c[g]	126.0 [1.6]	125.7 [6.2]	124.1[d] [−0.3]/116.6[e] [−7.8]	125.2[d] [5.7]/117.7[e] [−1.8]	n/c
[2, 6]	152.6 [−6.3]	152.9 [−1.5]	n/c	160.8 [1.9]	160.3 [7.4]	158.6[d] [−0.3]/149.6[e] [−9.3]	159.7[d] [6.8]/150.7[e] [−2.2]	n/c
[2, 7]	206.8 [−7.4]	207.1 [−1.9]	n/c	216.4 [2.2]	215.7 [8.6]	213.8[d] [−0.3]/203.3[e] [−10.9]	215.0[d] [7.9]/204.5[e] [−2.6]	n/c
[2, 8]	270.8 [−8.5]	n/c	n/c	281.8 [2.5]	n/c	278.8[d] [−0.4]/266.8[e] [−12.5]	n/c	n/c

Deviations from the corresponding atomization enthalpy approach results at the same level of theory as provided in Table 1 are given in brackets. Values are in kcal/mol

[a] Based on the reaction [2, n]polyprismane + 4n CH_4 → 3n C_2H_6 using $\Delta_f H^o_{(g)}$ of −17.8 kcal/mol [88, 89] and −20.1 kcal/mol [88, 89] for methane and ethane, respectively

[b] Based on the reaction [2, n]polyprismane + n/2 cyclohexane → n/2 adamantane using $\Delta_f H^o_{(g)}$ of −29.8 kcal/mol [90] and −32.1 kcal/mol [66, 91] for cyclohexane and adamantane, respectively

[c] Based on the reaction (4/n) [2, n]polyprismane → [2, 4]polyprismane

[d] Using an experimental [2, 4]polyprismane $\Delta_f H^o_{(g)}$ of 148.7 kcal/mol

[e] Using an experimental [2, 4]polyprismane $\Delta_f H^o_{(g)}$ of 142.7 kcal/mol

[f] Not applicable as the experimental $\Delta_f H^o_{(g)}$ for [2, 4]polyprismane is used in the homodesmic reaction scheme

[g] Not calculated due to computational expense for [2, n]polyprismane

[71], with the small difference between the two values due to our use of the more recent 1993 group additivity value updates [69]. Using the pre-1993 additivity values, we also obtain a Benson $\Delta_f H^o_{(g)}$ of 142.0 kcal/mol for this compound.

For the [m, n]polyprismanes, the ideal bond lengths and angles in the C–(H)(C)$_3$ and C–(C)$_4$ Benson constants do not accurately model the strained terminal C(CH)$_3$H (for $m = 2$) and C(C)(CH)$_2$H (for $m > 2$) groups or intrastack C(C)$_2$(CH)$_2$ (for units adjacent to the terminal rings where $m = 3$), C(C)$_3$(CH) (for units adjacent to the terminal rings where $m > 3$), and C(C)$_4$ (for units not adjacent to the terminal rings where $m > 5$; i.e., the central ring in [5, 3]polyprismane) functionalities present in these compounds. In addition, the cycloalkane rings present in [m, n]polyprismanes are planar with flat cage faces, whereas experimentally, the corresponding C$_4$ and higher cycloalkane rings upon which the Benson additivity values are developed (i.e., cyclobutane, cyclopentane, cyclohexane, etc.) are non-planar (e.g., chair conformation of cyclohexane). Consequently, there is a failure to incorporate the known [m, n]polyprismane non-classical bond angles and lengths in both the Benson carbon hybridization and ring approximation group additivity corrections, resulting in ever increasing deviations from high-level theoretical calculations using atomization, isodesmic, and/or homodesmic reaction schemes. Based on this rationale, the good agreement between the Benson and experimental $\Delta_f H^o_{(g)}$ for cubane is likely due to error cancelation, otherwise we would expect this additivity estimation approach to yield reasonably good agreement with the high level calculations for other [2, n]polyprismanes.

Gas-phase enthalpies ($\Delta_{acid} H^o_{(g)}$) and free energies ($\Delta_{acid} G^o_{(g)}$) of acid dissociation were also calculated for the [m, n]polyprismanes ($m = 2$; $m \times n \leq 16$) at the CBS-Q//B3, G4MP2, and G4 levels of theory (Table 4). All methods yielded $\Delta_{acid} H^o_{(g)}$ and $\Delta_{acid} G^o_{(g)}$ estimates within the corresponding experimental errors for cubane, the only polyprismane with experimental gas-phase acidity data. Among the several previous theoretical reports on the $\Delta_{acid} H^o_{(g)}$ for cubane, only the 'best theoretical estimate' by Ritchie et al. (406.3 kcal/mol; [35]) and the MP2/6-31 + G(d)//MP2/6-31 + G(d) estimate by Hare et al. (404.7 kcal/mol; [1]) are within the experimental error and in agreement with our CBS-Q//B3, G4MP2, and G4 estimates. To the best of our knowledge, no previous $\Delta_{acid} H^o_{(g)}$/$\Delta_{acid} G^o_{(g)}$ estimates have been reported for the [2, n] ($n = 3$, 5, 6, 7, 8) members, and no prior $\Delta_{acid} G^o_{(g)}$ theoretical estimate has been put forward for cubane.

Excellent agreement was also obtained between the three computational methods, with differences of no more than 1–1.5 kcal/mol for each compound. For the [2, 3] and [2, 4]polyprismanes with both CBS-Q//B3 and G4

Table 3 Gas-phase standard state (298.15 K, 1 atm) enthalpies of formation ($\Delta_f H^o_{(g)}$) for the [*m*, *n*]polyprismanes ($m \geq 2$; $m \times n \leq 16$) estimated using the Benson group additivity values (GAVs) from Cohen and Benson [69] and Sabbe et al. [70]

Deviations from the corresponding atomization enthalpy approach results at the CBS-Q//B3, G4MP2, and G4 levels of theory as provided in Table 1 are given in brackets

	Cohen and Benson [69] GAVs	Sabbe et al. [70]
[2, 3]	$121.4\ [-14.7_{\text{CBS-Q//B3}}, -10.8_{\text{G4MP2}}, -11.8_{\text{G4}}]$	$127.4\ [-8.7_{\text{CBS-Q//B3}}, -4.8_{\text{G4MP2}}, -5.8_{\text{G4}}]$
[2, 4]	$141.6\ [-7.3_{\text{CBS-Q//B3}}, -2.6_{\text{G4MP2}}, -3.6_{\text{G4}}]$	$148.2\ [-0.7_{\text{CBS-Q//B3}}, 4.0_{\text{G4MP2}}, 3.0]$
[2, 5]	$124.2\ [-0.2_{\text{CBS-Q//B3}}, 4.7_{\text{G4MP2}}]$	$132.8\ [8.4_{\text{CBS-Q//B3}}, 13.3_{\text{G4MP2}}]$
[2, 6]	$133.4\ [-25.5_{\text{CBS-Q//B3}}, -19.5_{\text{G4MP2}}]$	$143.1\ [-15.8_{\text{CBS-Q//B3}}, -9.8_{\text{G4MP2}}]$
[2, 7]	$167.6\ [-46.6_{\text{CBS-Q//B3}}, -39.5_{\text{G4MP2}}]$	$180.2\ [-34.0_{\text{CBS-Q//B3}}, -26.9_{\text{G4MP2}}]$
[2, 8]	$196.6\ [-82.7_{\text{CBS-Q//B3}}]$	$210.8\ [-68.5_{\text{CBS-Q//B3}}]$
[3, 3]	$229.8\ [-80.9_{\text{CBS-Q//B3}}, -73.8_{\text{G4MP2}}, -76.3_{\text{G4}}]$	$239.2\ [-71.5_{\text{CBS-Q//B3}}, -64.4_{\text{G4MP2}}, -66.9_{\text{G4}}]$
[3, 4]	$276.0\ [-107.2_{\text{CBS-Q//B3}}, -97.9_{\text{G4MP2}}]$	$286.4\ [-96.8_{\text{CBS-Q//B3}}, -87.5_{\text{G4MP2}}]$
[3, 5]	$265.8\ [-120.1_{\text{CBS-Q//B3}}, -109.6_{\text{G4MP2}}]$	$279.3\ [-106.6_{\text{CBS-Q//B3}}, -96.1_{\text{G4MP2}}]$
[4, 3]	$338.2\ [-139.9_{\text{CBS-Q//B3}}, -129.5_{\text{G4MP2}}]$	$351.0\ [-127.1_{\text{CBS-Q//B3}}, -116.7_{\text{G4MP2}}]$
[4, 4]	$410.4\ [-187.7_{\text{CBS-Q//B3}}, -173.5_{\text{G4MP2}}]$	$424.6\ [-173.5_{\text{CBS-Q//B3}}, -159.3_{\text{G4MP2}}]$
[5, 3]	$446.6\ [-196.5_{\text{CBS-Q//B3}}, -182.9_{\text{G4MP2}}]$	$462.8\ [-180.3_{\text{CBS-Q//B3}}, -166.7_{\text{G4MP2}}]$

Table 4 Gas-phase standard state (298.15 K, 1 atm) enthalpies ($\Delta_{\text{acid}}H^o_{(g)}$) and free energies ($\Delta_{\text{acid}}G^o_{(g)}$) of acid dissociation for the [*m*, *n*]polyprismanes ($m = 2$; $m \times n \leq 16$) at the CBS-Q//B3, G4MP2, and G4 levels of theory

	$\Delta_{\text{acid}}H^o_{(g)}$		$\Delta_{\text{acid}}G^o_{(g)}$	
	Current work	Literature	Current Work	Literature
[2, 3]	$401.4_{\text{CBS-Q//B3}}, 399.8_{\text{G4MP2}}, 401.1_{\text{G4}}$	n/a[a]	$393.5_{\text{CBS-Q//B3}}, 392.0_{\text{G4MP2}}, 393.2_{\text{G4}}$	n/a
[2, 4]	$407.2_{\text{CBS-Q//B3}}, 406.0_{\text{G4MP2}}, 406.9_{\text{G4}}$	$404 \pm 3_{\text{expt}}$ [1], 411.6_{AM1} [35], $442.5_{\text{SCF/6-31G}}$ [35], $440.5_{\text{SCF/6-31G*}}$ [35], $431.1_{\text{SCF/6-31+G}}$ [35], $429.2_{\text{SCF/6-31+G*}}$ [35], 416.9/$406.7_{\text{B3LYP/6-311+G**}}$ [2], $416.3_{\text{MP2/6-31+G}}$ [35], $406.3_{\text{'best' theoretical estimate}}$ [35], $404.7_{\text{MP2/6-31+G(d)//MP2/6-31+G(d)}}$ [1]	$399.3_{\text{CBS-Q//B3}}, 398.1_{\text{G4MP2}}, 399.0_{\text{G4}}$	$397 \pm 3_{\text{expt}}$ [1]
[2 ,5]	$406.6_{\text{CBS-Q//B3}}, 405.4_{\text{G4MP2}}$	n/a	$398.7_{\text{CBS-Q//B3}}, 397.5_{\text{G4MP2}}$	n/a
[2, 6]	$407.5_{\text{CBS-Q//B3}}, 406.6_{\text{G4MP2}}$	n/a	$399.5_{\text{CBS-Q//B3}}, 398.6_{\text{G4MP2}}$	n/a
[2, 7]	$406.3_{\text{CBS-Q//B3}}, 405.3_{\text{G4MP2}}$	n/a	$398.3_{\text{CBS-Q//B3}}, 397.3_{\text{G4MP2}}$	n/a
[2, 8]	$404.7_{\text{CBS-Q//B3}}$	n/a	$396.6_{\text{CBS-Q//B3}}$	n/a

Previous theoretical and experimental values reported in the literature are also provided. Subscripts indicate levels of theory or experimental values. Values are in kcal/mol

[a] Theoretical or experimental literature values not available

calculations, the two methods yielded respective $\Delta_{\text{acid}}H^o_{(g)}$ and $\Delta_{\text{acid}}G^o_{(g)}$ within 0.3 kcal/mol of each other. Thus, assuming G4 level $\Delta_{\text{acid}}H^o_{(g)}$ and $\Delta_{\text{acid}}G^o_{(g)}$ estimates to be the most accurate among the three methods, it appears that for the [2, *n*] ($n \geq 5$) compounds where only CBS-Q//B3 and G4MP2 calculations were completed, the CBS-Q//B3 results may be more accurate. Where three or more stacked rings were present (i.e., $m > 2$), geometry optimizations for the deprotonated anions converged on cage-opened non-prismatic geometries. This suggests that [≥3, *n*]polyprismanes may be structurally unstable to gas-phase deprotonation/protonation cycles, potentially precluding reliable experimental measurement or calculation of their acidities.

The [2, 3]polyprismane is more acidic (G4 $\Delta_{\text{acid}}G^o_{(g)}$= 393.2 kcal/mol) than its larger cycle [2, *n*]polyprismane (n = 4–8) counterparts (computational and experimental $\Delta_{\text{acid}}G^o_{(g)} \sim 397$ to 400 kcal/mol). This decreasing theoretical acidity trend between n = 3–4, and lack of a clear trend at $n \geq 4$, is consistent with the corresponding experimental trends in percent s-character of the C–H bonds (36% for [2, 3], 31% for [2, 4], and 30% for [2, 5]) as estimated from the J(^{13}C–H) NMR data [18]. Although the [2, 6] and higher [2,*n*]-polyprismanes are—at present—experimentally unknown, based on the gas-phase acidity calculations herein, we would expect the percent s-character of their C–H bonds to be approximately constant at ~30%.

Strain energies of [*m*, *n*]polyprismanes and other non-classical forms of carbon are of broad interest for correlating the structures of organic compounds with their stability and reactivity [72, 73]. Minyaev et al. were the first to systematically evaluate the strain in [*m*, *n*]polyprismanes using theoretical methods and a series of homodesmic reactions, and provide a detailed molecular orbital-based discussion of the values obtained [15]. Generalizing the stoichiometries of the homodesmic scheme used by these authors yields the following equation for predicting strain energy in any [m, n]polyprismane:

$$\begin{aligned}&(mn-2n)\,\mathrm{C(CH_3)_4}+(2n)\,\mathrm{(CH_3)_3CH}\\&\quad\rightarrow [m,n]\text{polyprismane}+(2mn-n)\mathrm{CH_3CH_3}\end{aligned}$$

In Table 5, we present the strain energies (both total strain and normalized per C–C bond) for the [m, n]polyprismanes ($m \geq 2$; n = 3–8; $m \times n \leq 16$) calculated at the CBS-Q//B3, G4MP2, and G4 levels, with comparison to previous reports in the literature. For the [2, n]polyprismanes (n = 2–6), where at least several prior estimates (including some high level QCISD(T), CBS, and Gaussian-n calculations for the [2, 3] and [2, 4] members) were available, our values are in excellent agreement and generally lie in the midpoint of the literature range. With all compounds, we observe little difference in predicted strain energies between the CBS-Q//B3, G4MP2, and G4 methods. The previous strain energy estimates for the stacked [m, n]polyprismanes ($m > 2$) at the B3LYP/6-311G(d,p) [15] ([3, 3], [3, 4], [3, 5], [4, 3], [4, 4]) and B3LYP/6-31G* [7] ([3, 4], [5, 3]) levels of theory range from about 14 to 20 kcal/mol less than our current CBS-Q//B3 and G4MP2 predictions. We see the same structure-strain trends as reported by Lewars [7], namely that total strain energies ($\mathrm{E_{str}}$) inevitably increase with larger [m,n]polyprismane size, and strain energies per one C–C bond ($\mathrm{E_{str}^{CC}}$) increase with increasing stack height within a given ring size series. Within a given stack height, $\mathrm{E_{str}^{CC}}$ reaches a minimum with a ring size of five, increasing with either decreasing or increasing ring size away from this minima.

We know generally that while compounds with large strain energies are susceptible to exothermic reactions such as combustion and strain lowering intramolecular rearrangements and disproportionations (i.e., thermodynamic instability), there is no straightforward correlation between strain energy and kinetic stability [7]. Thus, cubane is known to be “extraordinarily stable” in contrast to many substantially less strained compounds [17, 74]. If $\mathrm{E_{str}^{CC}}$ does correlate with kinetic stability for the [m, n]polyprismanes, we would expect the [2, 5], [2, 6], [2, 7], and [2, 8] members to be significantly more stable than cubane, and some stacked members (e.g., [3, 5]) to be about as stable as prismane ([2, 3]). With regard to thermodynamic stability, the predicted relative invariance of gas-phase acidities for $m > 4$ with the [2, m]polyprismanes results in no significant correlation with either E_{str} or $E_{\mathrm{str}}^{\mathrm{CC}}$. Thus, equilibrium constants for gas-phase deprotonation of [m, n]polyprismanes do not appear to correlate with molecular strain.

As discussed by Wiberg [73], a priori expectations that increased strain leads to increased reactivity are not always realized. The location of the activated complex along the reaction coordinate and the strain energies of reactants and products must be taken into consideration. For example, where the structure of the activated complex resembles the highly strained reactants, only a small quantity of strain energy is released in the rate determining step, and hence there is little change in rate constant with increasing reactant strain. In addition, where the products or intermediates are also highly strained, there is little driving force for the reaction (either in kinetic or thermodynamic terms). Upon deprotonation, substantial changes in geometry to the [m, n]polyprismanic carbon cages and carbon-hydrogen bond lengths and angles are expected (Fig. 2 and Table 6). As with the calculations on the undissociated molecular forms, little difference in gas-phase anion geometry is predicted (bond lengths within ~±0.001–0.002 Å, bond angles within ~±0.1–0.2°) between the CBS-Q//B3, G4MP2, and G4 levels of theory. The anions have significantly longer carbon-hydrogen bonds compared to the molecular species (~1.08 to 1.09 Å → 1.10 to 1.11 Å), and this lengthening is approximately uniform around the cage. The hydrogen atoms are also generally angled away asymmetrically from the reaction center, an effect whose magnitude decreases with increasing through-bond distance from the carbanion.

Concomitant with these changes, the internal angles of the carbon framework contract about the reaction center for the [2, 3] through [2, 6] members, increasing the s-character of the carbanion to better accommodate the negative charge. In contrast, all the [2,8]polyprismane internuclear angles at the carbanion increase upon deprotonation. For the [2, 7] member, the internuclear angle between the carbanion center and the adjacent carbon atoms in the same ring ($\angle \mathrm{C_2C_1C}_n$) decreases, but the internuclear angle between the carbon center, either adjacent carbon atom in the same ring, and the carbon directly above the reaction center in the stack ($\angle \mathrm{C_2C_1C_{1'}}=\angle \mathrm{C}_n\mathrm{C_1C_{1'}}$) increases. The CBS-Q//B3 $\angle \mathrm{C_2C_1C}_n$ gas-phase angular contractions ($\Delta\angle \mathrm{C_2C_1C}_n$) about the reaction center due to deprotonation are as follows: [2, 3], −2.3°; [2, 4], −3.0°; [2, 5], −3.3°; [2, 6], −3.3°; [2, 7], −1.4°; and [2, 8], +2.4°. We find excellent agreement in the CBS-Q//B3 $\Delta\angle \mathrm{C_2C_1C_4}$ of −3.0° for cubane and the SCF/6-31+G* estimate of −3.5° by Ritchie and Bachrach [35], who also noted that unlike other formal sp^3 centers, cubane is anomalous and behaves more like a formal sp^2 center. Using the INDO-LMO method, So et al. [75] reported $\Delta\angle \mathrm{C_2C_1C}_n$ of −0.4° [2, 3], −2.9° [2, 4], and −3.0° [2, 5] following gas-phase deprotonation for these three [2,n]polyprismanes, which—with the exception of prismane—are also in excellent agreement with our calculations.

In the molecular forms, all [2,n]polyprismane (n = 3–8) $\angle \mathrm{C_2C_1C_{1'}}/\angle \mathrm{C}_n\mathrm{C_1C_{1'}}$ are 90.0°. Deprotonation yields the

Table 5 Total strain energies (E_{str}) and strain energies per one C–C bond ($E_{\mathrm{str}}^{\mathrm{CC}}$) for the [$m$, n]polyprismanes ($m \geq 2$; $m \times n \leq 16$) at the CBS-Q//B3, G4MP2, and G4 levels of theory

	E_{str}		$E_{\mathrm{str}}^{\mathrm{CC}}$	
	Current work	Literature	Current work	Literature
[2, 3]	$142.0_{\mathrm{CBS\text{-}Q//B3}}$, 142.3_{G4MP2}, 141.8_{G4}	$136_{\mathrm{B3LYP/6\text{-}311G(2df,p)}}$ [15], 148.2 [29][a], $145.3_{\mathrm{HF/6\text{-}31G*}}$ [92], $148.7_{\mathrm{SCF/6\text{-}31G*}}$ [78], 145.1_{G3B3LYP} [81], 161.6_{G3MP2} [85], $143.8_{\mathrm{QCISD(T)/6\text{-}311+(2df,p)//MP2/6\text{-}311(d,p}}$ [4], $121.7_{\mathrm{B3LYP/6\text{-}311+(3df,2p)//B3LYP/6\text{-}311G(d,p)}}$ [4], $146.3_{\mathrm{MP2/6\text{-}311G(d,p)//MP2/6\text{-}311G(d,p)}}$ [4], $146.1_{\mathrm{MP4/6\text{-}311G(d,p)//MP4/6\text{-}311G(d,p)}}$ [4], $124.0_{\mathrm{CBS\text{-}4}}$ [4], $142.1_{\mathrm{CBS\text{-}Q}}$ [4], 143.4_{G1} [4], 141.9_{G2} [4]	$15.8_{\mathrm{CBS\text{-}Q//B3}}$, 15.8_{G4MP2}, 15.7_{G4}	$15.1_{\mathrm{B3LYP/6\text{-}311G(2df,p)}}$ [15], 16.5 [29], $16.1_{\mathrm{HF/6\text{-}31G*}}$ [92], $16.5_{\mathrm{SCF/6\text{-}31G*}}$ [78], 16.1_{G3B3LYP} [81], 18.0_{G3MP2} [85], $16.0_{\mathrm{QCISD(T)/6\text{-}311+(2df,p)//MP2/6\text{-}311(d,p)}}$ [4], $13.5_{\mathrm{B3LYP/6\text{-}311+(3df,2p)//B3LYP/6\text{-}311G(d,p)}}$ [4], $16.3_{\mathrm{MP2/6\text{-}311G(d,p)//MP2/6\text{-}311G(d,p)}}$ [4], $16.2_{\mathrm{MP4/6\text{-}311G(d,p)//MP4/6\text{-}311G(d,p)}}$ [4], $13.8_{\mathrm{CBS\text{-}4}}$ [4], $15.8_{\mathrm{CBS\text{-}Q}}$, 15.9_{G1} [4], 15.8_{G2} [4]
[2, 4]	$157.0_{\mathrm{CBS\text{-}Q//B3}}$, 157.7_{G4MP2}, 156.9_{G4}	157[b] [47], $151_{\mathrm{B3LYP/6\text{-}311G(2df,p)}}$ [15], 157.9 [29], 154.7 [73][c], $158.6_{\mathrm{HF/6\text{-}31G*}}$ [92], $169.1_{\mathrm{B3LYP/6\text{-}31G*}}$ [93], $165.9^{\mathrm{d}}_{\mathrm{MM}}$ [94], $166.9^{\mathrm{e}}_{\mathrm{MM}}$ [94], $164.9_{\mathrm{SCF/6\text{-}31G*}}$ [78], $165.4_{\mathrm{MP2/6\text{-}311G(d,p)}}$ [4], $162.8 \pm 2.3_{\mathrm{G2(MP2),G2,G3//B3LYP,G3[avg],isodesmic}}$ [86], $160.3 \pm 2.2_{\mathrm{G2(MP2),G2,G3//B3LYP,G3[avg]}}$ [86], $163.8_{\mathrm{MP2(FULL)/6\text{-}31G(d)}}$ [86], 161.3[e] [87], $153.7_{\mathrm{B3LYP/6\text{-}31G*}}$ [7]	$13.1_{\mathrm{CBS\text{-}Q//B3}}$, 13.2_{G4MP2}, 13.1_{G4}	13.1[b] [47], $12.6_{\mathrm{B3LYP/6\text{-}311G(2df,p)}}$ [15], 13.2 [29], 12.9 [73], $13.2_{\mathrm{HF/6\text{-}31G*}}$ [92], $14.1_{\mathrm{B3LYP/6\text{-}31G*}}$ [93], $13.8^{\mathrm{c}}_{\mathrm{MM}}$ [94], $13.9^{\mathrm{d}}_{\mathrm{MM}}$ [94], $13.7_{\mathrm{SCF/6\text{-}31G*}}$ [78], $13.8_{\mathrm{MP2/6\text{-}311G(d,p)}}$ [4], $13.6 \pm 0.2_{\mathrm{G2(MP2),G2,G3//B3LYP,G3[avg],isodesmic}}$ [86], $13.4 \pm 0.2_{\mathrm{G2(MP2),G2,G3//B3LYP,G3[avg]}}$ [86], $13.6_{\mathrm{MP2(FULL)/6\text{-}31G(d)}}$ [86], 13.4[e] [87], $12.8_{\mathrm{B3LYP/6\text{-}31G*}}$ [7]
[2, 5]	$134.6_{\mathrm{CBS\text{-}Q//B3}}$, 136.7_{G4MP2}	$129_{\mathrm{B3LYP/6\text{-}311G(2df,p)}}$ [15], 142.9 [29], $140.1_{\mathrm{SCF/6\text{-}31G*}}$ [78]	$9.0_{\mathrm{CBS\text{-}Q//B3}}$, 9.1_{G4MP2}	$8.6_{\mathrm{B3LYP/6\text{-}311G(2df,p)}}$ [15], 9.5 [29], $9.3_{\mathrm{SCF/6\text{-}31G*}}$ [78]
[2, 6]	$171.2_{\mathrm{CBS\text{-}Q//B3}}$, 173.6_{G4MP2}	$163_{\mathrm{B3LYP/6\text{-}311G(2df,p)}}$) [15], 180.1 [29], $177.7_{\mathrm{SCF/6\text{-}31G*}}$ [78]	$9.6_{\mathrm{CBS\text{-}Q//B3}}$, 9.7_{G4MP2}	$9.1_{\mathrm{B3LYP/6\text{-}311G(2df,p)}}$ [15], 10.0 [29], $9.9_{\mathrm{SCF/6\text{-}31G*}}$ [78]
[2, 7]	$228.7_{\mathrm{CBS\text{-}Q//B3}}$, 231.3_{G4MP2}	242.1 [29], $240.7_{\mathrm{SCF/6\text{-}31G*}}$ [78]	$10.9_{\mathrm{CBS\text{-}Q//B3}}$, 11.0_{G4MP2}	11.5 [29], $11.5_{\mathrm{SCF/6\text{-}31G*}}$ [78]
[2, 8]	$295.9_{\mathrm{CBS\text{-}Q//B3}}$	315.5 [29], $315.9_{\mathrm{SCF/6\text{-}31G*}}$ [78]	$12.3_{\mathrm{CBS\text{-}Q//B3}}$	13.1 [29], $13.2_{\mathrm{SCF/6\text{-}31G*}}$ [78]
[3, 3]	$313.4_{\mathrm{CBS\text{-}Q//B3}}$, 313.6_{G4MP2}, 313.6_{G4}	$298_{\mathrm{B3LYP/6\text{-}311G(d,p)}}$ [15]	$20.9_{\mathrm{CBS\text{-}Q//B3}}$, 20.9_{G4MP2}, 20.9_{G4}	$19.9_{\mathrm{B3LYP/6\text{-}311G(d,p)}}$ [15]
[3, 4]	$387.0_{\mathrm{CBS\text{-}Q//B3}}$, 387.4_{G4MP2}	$373_{\mathrm{B3LYP/6\text{-}311G(d,p)}}$ [15], $378.8_{\mathrm{B3LYP/6\text{-}31G*}}$ [7]	$19.4_{\mathrm{CBS\text{-}Q//B3}}$, 19.4_{G4MP2}	$18.7_{\mathrm{B3LYP/6\text{-}311G(d,p)}}$ [15], $18.9_{\mathrm{B3LYP/6\text{-}31G*}}$ [7]
[3, 5]	$390.7_{\mathrm{CBS\text{-}Q//B3}}$, 392.5_{G4MP2}	$378_{\mathrm{B3LYP/6\text{-}311G(d,p)}}$ [15]	$15.6_{\mathrm{CBS\text{-}Q//B3}}$, 15.7_{G4MP2}	$15.1_{\mathrm{B3LYP/6\text{-}311G(d,p)}}$ [15]
[4, 3]	$477.6_{\mathrm{CBS\text{-}Q//B3}}$, 477.7_{G4MP2}	$457_{\mathrm{B3LYP/6\text{-}311G(d,p)}}$ [15]	$22.8_{\mathrm{CBS\text{-}Q//B3}}$, 22.8_{G4MP2}	$21.8_{\mathrm{B3LYP/6\text{-}311G(d,p)}}$ [15]
[4, 4]	$597.5_{\mathrm{CBS\text{-}Q//B3}}$, 597.4_{G4MP2}	$579_{\mathrm{B3LYP/6\text{-}311G(d,p)}}$ [15]	$21.4_{\mathrm{CBS\text{-}Q//B3}}$, 21.4_{G4MP2}	$20.7_{\mathrm{B3LYP/6\text{-}311G(d,p)}}$ [15]
[5, 3]	$639.3_{\mathrm{CBS\text{-}Q//B3}}$, 639.5_{G4MP2}	$619.5_{\mathrm{B3LYP/6\text{-}31G*}}$ [7][a]	$23.7_{\mathrm{CBS\text{-}Q//B3}}$, 23.7_{G4MP2}	$22.9_{\mathrm{B3LYP/6\text{-}31G*}}$ [7][a]

Previous estimates reported in the literature are also provided. Subscripts indicate levels of theory. Values are in kcal/mol

[a] Calculated in [28] using theoretical $\Delta_f H^o_{(g)}$ (estimated at an unclear level of theory, either HF/6-31G*, MP2/6-31G*, or B3LYP/6-31G*, or some combination thereof; the experimental $\Delta_f H^o_{(g)}$ was used for cubane by these authors) using Benson increments to the $\Delta_f H^o_{(g)}$ corresponding to various structural fragments in aliphatic hydrocarbons

[b] Calculated using Franklin's method of group equivalents and the experimental $\Delta_f H^o_{(g)}$

[c] Calculated from experimental $\Delta_f H^o_{(g)}$

[d] Molecular mechanics with the Schleyer force field and Allinger force field

[e] Calculated using the Domalski and Hearing strain-free group contribution values and the experimental $\Delta_f H^o_{(g)}$

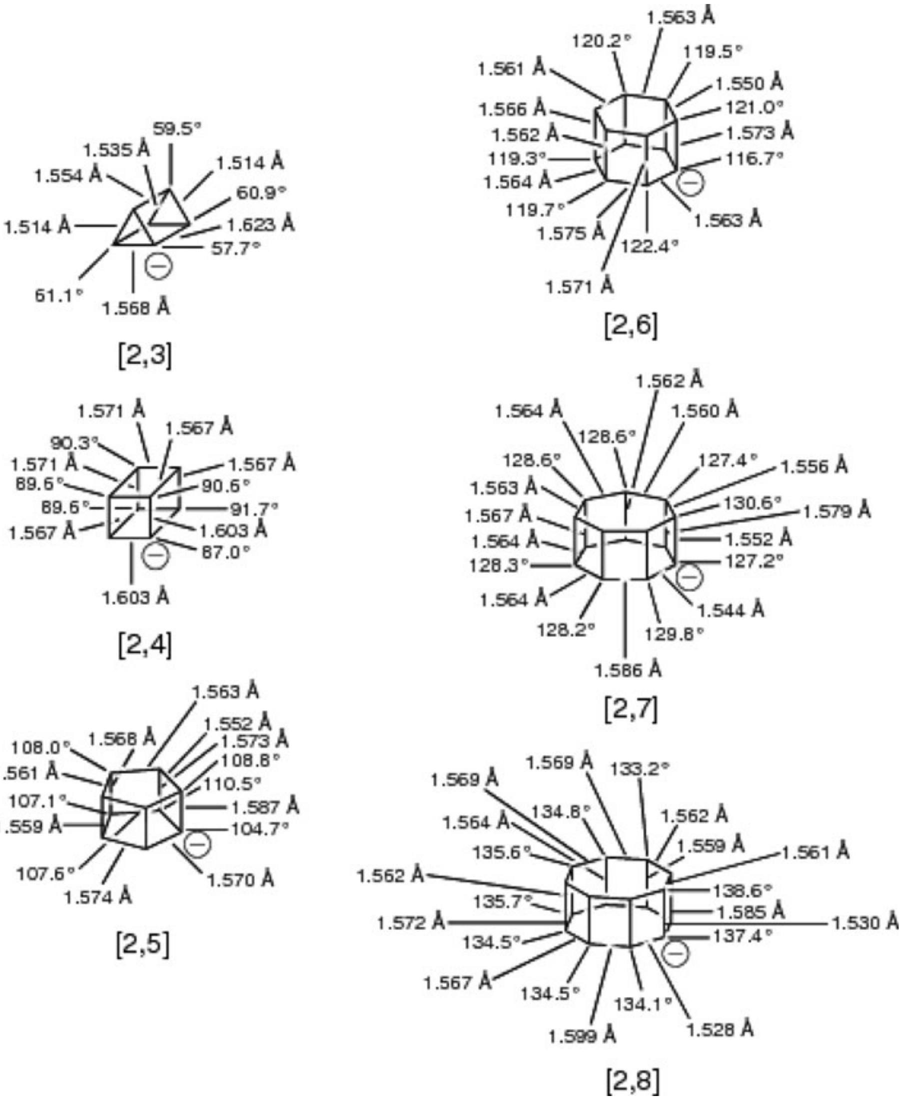

Fig. 2 Structures with gas-phase standard state (298.15 K, 1 atm) CBS-Q//B3 optimized bond lengths and angles for the deprotonated [*m*, *n*]polyprismane ($m = 2$; $n = 3$–8; $m \times n \leq 16$) anions

following $\Delta\angle C_2C_1C_{1'}/\Delta\angle C_nC_1C_{1'}$, which consistently increase with increasing ring size: [2, 3], −4.8°; [2, 4], −3.0°; [2, 5], −1.6°; [2, 6], −0.6°; [2, 7], +1.2°; and [2, 8], +2.9°. Consequently, upon gas-phase deprotonation, the CBS-QB//3 calculations (as well as G4MP2 [$n = 3$–7] and G4 [$n = 3, 4$]) show rehybridization at the anionic center to increased s-character for [2,*n*]polyprismanes for $n = 3$–6, reflected in internuclear angular contraction about the carbanion, consistent with expectations previously discussed in the literature [35, 75, 76]. Further work is needed to better understand the predicted internuclear angle expansions about the reaction center during gas-phase deprotonation of the [2, 7] and [2, 8]polyprismanes, as well as studies of the larger ring members at $n \geq 9$. Overall, we observe no clear decrease in strain upon deprotonation, despite significant geometrical changes, consistent with the predicted insensitivity of gas-phase acidity toward variability in total and normalized strain among the [*m*,*n*]polyprismanes.

4 Conclusions

Gas-phase standard state enthalpies of formation and enthalpies and free energies of acid dissociation calculated at the CBS-Q//B3, G4MP2, and G4 levels of theory for [*m*, *n*]polyprismanes ($m \geq 2$; $n = 3$–8; $m \times n \leq 16$) yield qualitatively consistent intermethod results with modest intermethod quantitative variability that increases with increasing molecular size. In particular, the lower cost CBS-Q//B3 method yields effectively equivalent gas-phase acidity estimates as the G4MP2 and G4 methods for these compounds, facilitating its use for larger members of the [*m*, *n*]polyprismane class. Enthalpies of formation calculated using the atomization method are increasingly overestimated by the CBS-Q//B3 method with larger [*m*, *n*]polyprismane sizes, necessitating the use of G4MP2 or G4 calculations for accurate estimates. However, beyond $m \times n$=15, G4MP2 calculations were prohibitively expensive, and G4 calculations were only feasible up to

Table 6 Estimated gas-phase standard state (298.15 K, 1 atm) carbon–hydrogen bond lengths ($r_{\mathrm{C-H}}$) and bond angles at the CBS-Q//B3 level of theory for the deprotonated anion forms of the [*m*, *n*]polyprismanes ($m = 2$; $m \times n \leq 16$)

Stack		C_1–H		C_2–H		C_3–H		C_4–H		C_5–H		C_6–H		C_7–H		C_8–H	
		$r_{\mathrm{C1-H}}$	Angle	$r_{\mathrm{C2-H}}$	Angle	$r_{\mathrm{C3-H}}$	Angle	$r_{\mathrm{C4-H}}$	Angle	$r_{\mathrm{C5-H}}$	Angle	$r_{\mathrm{C6-H}}$	Angle	$r_{\mathrm{C7-H}}$	Angle	$r_{\mathrm{C8-H}}$	Angle
[2, 3]	1	Anion	Anion	1.093 Å	129.1°$_{\mathrm{C1-C2-H}}$ 130.2°$_{\mathrm{C3-C2-H}}$ 130.3°$_{\mathrm{C2'-C2-H}}$	1.093 Å	129.1°$_{\mathrm{C1-C3-H}}$ 130.2°$_{\mathrm{C2-C3-H}}$ 130.3°$_{\mathrm{C3'-C3-H}}$	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
	2	1.093 Å	127.8°$_{\mathrm{C2'-C1'-H}}$ 127.8°$_{\mathrm{C3'-C1'-H}}$ 132.1°$_{\mathrm{C1-C1'-H}}$	1.093 Å	129.1°$_{\mathrm{C1'-C2'-H}}$ 130.2°$_{\mathrm{C3'-C2'-H}}$ 130.3°$_{\mathrm{C2-C2'-H}}$	1.093 Å	129.1°$_{\mathrm{C1'-C3'-H}}$ 130.2°$_{\mathrm{C2'-C3'-H}}$ 130.3°$_{\mathrm{C3-C3'-H}}$	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
[2, 4]	1	Anion	Anion	1.103 Å	125.5°$_{\mathrm{C1-C2-H}}$ 123.7°$_{\mathrm{C3-C2-H}}$ 123.7°$_{\mathrm{C2'-C2-H}}$	1.103 Å	126.8°$_{\mathrm{C2-C3-H}}$ 126.7°$_{\mathrm{C4-C3-H}}$ 123.1°$_{\mathrm{C3'-C3-H}}$	1.103 Å	125.5°$_{\mathrm{C1-C4-H}}$ 123.7°$_{\mathrm{C3-C4-H}}$ 123.7°$_{\mathrm{C4'-C4-H}}$	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
	2	1.103 Å	123.7°$_{\mathrm{C2'-C1'-H}}$ 123.7°$_{\mathrm{C4'-C1'-H}}$ 125.5°$_{\mathrm{C1-C1'-H}}$	1.103 Å	126.8°$_{\mathrm{C1'-C2'-H}}$ 123.2°$_{\mathrm{C3'-C2'-H}}$ 126.8°$_{\mathrm{C2-C2'-H}}$	1.095 Å	125.1°$_{\mathrm{C2'-C3'-H}}$ 125.1°$_{\mathrm{C4'-C3'-H}}$ 125.1°$_{\mathrm{C3-C3'-H}}$	1.103 Å	126.8°$_{\mathrm{C1'-C4'-H}}$ 123.2°$_{\mathrm{C3'-C4'-H}}$ 126.8°$_{\mathrm{C4-C4'-H}}$	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
[2, 5]	1	Anion	Anion	1.103 Å	121.1°$_{\mathrm{C1-C2-H}}$ 115.8°$_{\mathrm{C3-C2-H}}$ 122.6°$_{\mathrm{C2'-C2-H}}$	1.098 Å	120.8°$_{\mathrm{C2-C3-H}}$ 119.4°$_{\mathrm{C4-C3-H}}$ 122.5°$_{\mathrm{C3'-C3-H}}$	1.098 Å	120.8°$_{\mathrm{C3-C4-H}}$ 119.4°$_{\mathrm{C5-C4-H}}$ 122.5°$_{\mathrm{C4'-C4-H}}$	1.103 Å	121.1°$_{\mathrm{C1-C5-H}}$ 115.8°$_{\mathrm{C4-C5-H}}$ 122.6°$_{\mathrm{C5'-C5-H}}$	n/a	n/a	n/a	n/a	n/a	n/a
	2	1.104 Å	118.3°$_{\mathrm{C2'-C1'-H}}$ 118.3°$_{\mathrm{C5'-C1'-H}}$ 123.6°$_{\mathrm{C1-C1'-H}}$	1.101 Å	121.1°$_{\mathrm{C1'-C2'-H}}$ 117.4°$_{\mathrm{C3'-C2'-H}}$ 124.7°$_{\mathrm{C2-C2'-H}}$	1.095 Å	119.4°$_{\mathrm{C2'-C3'-H}}$ 119.1°$_{\mathrm{C4'-C3'-H}}$ 123.3°$_{\mathrm{C3-C3'-H}}$	1.095 Å	119.4°$_{\mathrm{C3'-C4'-H}}$ 119.1°$_{\mathrm{C5'-C4'-H}}$ 123.3°$_{\mathrm{C4-C4'-H}}$	1.101 Å	121.1°$_{\mathrm{C1'-C5'-H}}$ 117.4°$_{\mathrm{C4'-C5'-H}}$ 124.7°$_{\mathrm{C5-C5'-H}}$	n/a	n/a	n/a	n/a	n/a	n/a
[2, 6]	1	Anion	Anion	1.106 Å	117.6°$_{\mathrm{C1-C2-H}}$ 111.4°$_{\mathrm{C3-C2-H}}$ 121.1°$_{\mathrm{C2'-C2-H}}$	1.097 Å	116.3°$_{\mathrm{C2-C3-H}}$ 114.7°$_{\mathrm{C4-C3-H}}$ 120.9°$_{\mathrm{C3'-C3-H}}$	1.095 Å	115.7°$_{\mathrm{C3-C4-H}}$ 115.7°$_{\mathrm{C5-C4-H}}$ 121.2°$_{\mathrm{C4'-C4-H}}$	1.097 Å	116.3°$_{\mathrm{C4-C5-H}}$ 114.7°$_{\mathrm{C6-C5-H}}$ 120.9°$_{\mathrm{C5'-C5-H}}$	1.106 Å	117.6°$_{\mathrm{C1-C6-H}}$ 111.4°$_{\mathrm{C5-C6-H}}$ 121.1°$_{\mathrm{C6'-C6-H}}$	n/a	n/a	n/a	n/a
	2	1.109 Å	114.3°$_{\mathrm{C2'-C1'-H}}$ 114.3°$_{\mathrm{C6'-C1'-H}}$ 122.2°$_{\mathrm{C1-C1'-H}}$	1.102 Å	116.6°$_{\mathrm{C1'-C2'-H}}$ 113.7°$_{\mathrm{C3'-C2'-H}}$ 122.5°$_{\mathrm{C2-C2'-H}}$	1.095 Å	115.5°$_{\mathrm{C2'-C3'-H}}$ 114.6°$_{\mathrm{C4'-C3'-H}}$ 121.4°$_{\mathrm{C3-C3'-H}}$	1.096 Å	115.4°$_{\mathrm{C3'-C4'-H}}$ 115.4°$_{\mathrm{C5'-C4'-H}}$ 121.6°$_{\mathrm{C4-C4'-H}}$	1.095 Å	115.5°$_{\mathrm{C4'-C5'-H}}$ 114.6°$_{\mathrm{C6'-C5'-H}}$ 121.4°$_{\mathrm{C5-C5'-H}}$	1.102 Å	116.6°$_{\mathrm{C1'-C6'-H}}$ 113.7°$_{\mathrm{C5'-C6'-H}}$ 122.5°$_{\mathrm{C6-C6'-H}}$	n/a	n/a	n/a	n/a
[2, 7]	1	Anion	Anion	1.109 Å	116.4°$_{\mathrm{C1-C2-H}}$ 107.7°$_{\mathrm{C3-C2-H}}$ 119.8°$_{\mathrm{C2'-C2-H}}$	1.099 Å	112.8°$_{\mathrm{C2-C3-H}}$ 112.1°$_{\mathrm{C4-C3-H}}$ 119.1°$_{\mathrm{C3'-C3-H}}$	1.096 Å	112.7°$_{\mathrm{C3-C4-H}}$ 112.0°$_{\mathrm{C5-C4-H}}$ 119.4°$_{\mathrm{C4'-C4-H}}$	1.096 Å	112.7°$_{\mathrm{C4-C5-H}}$ 112.0°$_{\mathrm{C6-C5-H}}$ 119.4°$_{\mathrm{C5'-C5-H}}$	1.099 Å	112.8°$_{\mathrm{C5-C6-H}}$ 112.1°$_{\mathrm{C7-C6-H}}$ 119.1°$_{\mathrm{C6'-C6-H}}$	1.109 Å	116.4°$_{\mathrm{C1-C7-H}}$ 107.7°$_{\mathrm{C6-C7-H}}$ 119.8°$_{\mathrm{C7'-C7-H}}$	n/a	n/a
	2	1.113 Å	111.1°$_{\mathrm{C2'-C1'-H}}$ 111.1°$_{\mathrm{C7'-C1'-H}}$ 121.0°$_{\mathrm{C1-C1'-H}}$	1.102 Å	113.5°$_{\mathrm{C1'-C2'-H}}$ 111.2°$_{\mathrm{C3'-C2'-H}}$ 120.7°$_{\mathrm{C2-C2'-H}}$	1.095 Å	112.7°$_{\mathrm{C2'-C3'-H}}$ 111.2°$_{\mathrm{C4'-C3'-H}}$ 119.7°$_{\mathrm{C3-C3'-H}}$	1.096 Å	112.4°$_{\mathrm{C3'-C4'-H}}$ 111.9°$_{\mathrm{C5'-C4'-H}}$ 119.7°$_{\mathrm{C4-C4'-H}}$	1.096 Å	112.4°$_{\mathrm{C4'-C5'-H}}$ 111.9°$_{\mathrm{C6'-C5'-H}}$ 119.7°$_{\mathrm{C5-C5'-H}}$	1.095 Å	112.7°$_{\mathrm{C5'-C6'-H}}$ 111.2°$_{\mathrm{C7'-C6'-H}}$ 119.7°$_{\mathrm{C6-C6'-H}}$	1.102 Å	113.5°$_{\mathrm{C1'-C7'-H}}$ 111.2°$_{\mathrm{C6'-C7'-H}}$ 120.7°$_{\mathrm{C7-C7'-H}}$	n/a	n/a
[2, 8]	1	Anion	Anion	1.111 Å	115.8°$_{\mathrm{C1-C2-H}}$ 105.3°$_{\mathrm{C3-C2-H}}$ 119.5°$_{\mathrm{C2'-C2-H}}$	1.098 Å	110.0°$_{\mathrm{C2-C3-H}}$ 109.8°$_{\mathrm{C4-C3-H}}$ 118.3°$_{\mathrm{C3'-C3-H}}$	1.096 Å	110.4°$_{\mathrm{C3-C4-H}}$ 109.3°$_{\mathrm{C5-C4-H}}$ 118.6°$_{\mathrm{C4'-C4-H}}$	1.096 Å	109.4°$_{\mathrm{C4-C5-H}}$ 109.4°$_{\mathrm{C6-C5-H}}$ 118.3°$_{\mathrm{C5'-C5-H}}$	1.096 Å	110.4°$_{\mathrm{C5-C6-H}}$ 109.3°$_{\mathrm{C7-C6-H}}$ 118.6°$_{\mathrm{C6'-C6-H}}$	1.098 Å	110.0°$_{\mathrm{C6-C7-H}}$ 109.8°$_{\mathrm{C8-C7-H}}$ 118.3°$_{\mathrm{C7'-C7-H}}$	1.111 Å	115.8°$_{\mathrm{C1-C8-H}}$ 105.3°$_{\mathrm{C7-C8-H}}$ 119.5°$_{\mathrm{C8'-C8-H}}$
	2	1.119 Å	108.2°$_{\mathrm{C2'-C1'-H}}$ 108.2°$_{\mathrm{C8'-C1'-H}}$ 120.2°$_{\mathrm{C1-C1'-H}}$	1.102 Å	111.2°$_{\mathrm{C1'-C2'-H}}$ 109.2°$_{\mathrm{C3'-C2'-H}}$ 119.8°$_{\mathrm{C2-C2'-H}}$	1.095 Å	110.2°$_{\mathrm{C2'-C3'-H}}$ 108.7°$_{\mathrm{C4'-C3'-H}}$ 118.7°$_{\mathrm{C3-C3'-H}}$	1.096 Å	110.0°$_{\mathrm{C3'-C4'-H}}$ 109.3°$_{\mathrm{C5'-C4'-H}}$ 118.8°$_{\mathrm{C4-C4'-H}}$	1.096 Å	109.4°$_{\mathrm{C4'-C5'-H}}$ 109.4°$_{\mathrm{C6'-C5'-H}}$ 118.5°$_{\mathrm{C5-C5'-H}}$	1.096 Å	110.0°$_{\mathrm{C5'-C6'-H}}$ 109.3°$_{\mathrm{C7'-C6'-H}}$ 118.8°$_{\mathrm{C6-C6'-H}}$	1.095 Å	110.2°$_{\mathrm{C6'-C7'-H}}$ 108.7°$_{\mathrm{C8'-C7'-H}}$ 118.7°$_{\mathrm{C7-C7'-H}}$	1.102 Å	111.2°$_{\mathrm{C1'-C8'-H}}$ 109.2°$_{\mathrm{C7'-C8'-H}}$ 119.8°$_{\mathrm{C8-C8'-H}}$

The numbering system for carbon atoms proceeds starting at 1 (carbanion) and increasing sequentially clockwise around each ring with "′" denotation for adjacent carbon atoms in the second stack

$m \times n = 9$. Various isodesmic and homodesmic reaction schemes at these levels of theory do not offer any clear prediction advantage over the atomization method. Good agreement with previous DFT formation enthalpy estimates in the literature obtained using homodesmic approaches suggests the thermochemistry of larger [*m*, *n*]polyprismanes may be studied using these methods and lower cost levels of theory. Group additivity methods yield, at present, inaccurate enthalpies of formation for [*m*, *n*]polyprismanes due to the absence of appropriate strain correction factors.

Geometry optimizations for the deprotonated anions converged on cage-opened non-prismatic geometries where three or more stacked [*m*, *n*]polyprismane rings were present. These compounds may be structurally unstable to gas-phase deprotonation/protonation cycles, potentially preventing reliable experimental measurement or calculation of their acidities. Good correlations were found between the gas-phase acidities of the [2,3], [2,4], and [2,5]polyprismanes and percent s-character of the C–H bonds. Calculations indicate no substantial change in the gas-phase acidity for the [2, *n*]polyprismanes at $n \geq 6$, suggesting no corresponding change in C–H bond s-character over this range. Larger [*m*, *n*]polyprismanes have higher total strain energies. Increasing stack height within a given ring size series results in larger strain energies per one C–C bond, which also reach a minimum with a ring size of five within a given stack height. Gas-phase deprotonation results in substantial geometry changes between the molecular and deprotonated anionic forms. Contraction of the internuclear angles about the reaction center occurs for the [2, 3]–[2, 6] members as a result of rehybridization to increase s-character in the carbanion and better accommodate the negative charge. Neither total energy nor per carbon–carbon bond strain energies correlate with gas-phase acidity, likely because deprotonation does not relieve significant molecular strain.

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