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The Thermodynamic Stability of P_8, A CBS-Q Study

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ABSTRACT: *The thermodynamic stabilities of P_2, P_4, and three P_8 cage structure were investigated through high-precision CBS-Q calculations. The CBS-Q values for the bond energy of P_2 (ΔE_o : +115.7 kcal mol^{-1}) and the formation of P_4 from P_2 (ΔE_o : −56.6 kcal mol^{-1}) were in excellent agreement with the experimental values (E_o : +117 and −56.4 kcal mol^{-1} respectively). Among the P_8 cages, the cubane structure was the least stable (ΔE_o +37 kcal vs. $2\times P_4$). The most stable P_8 isomer adopts a cuneane structure resembling S_4N_4, and is more stable than white phosphorus at T = 0 K (ΔE_o −3.3 kcal mol^{-1}), but still unstable under standard conditions for entropic reasons (ΔG^o of +8.1 kcal mol^{-1} vs. $2\times P_4$). The CBS-Q energies represent significant revisions (6–20 kcal mol^{-1}) of previous computational predictions obtained by high-level single method calculations.* Heteroatom Chem 16:453–457, 2005;
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INTRODUCTION

The synthesis of new allotropes of phosphorus based on molecular P_n cage structures beyond white phosphorus (P_4) has been a subject of considerable interest over the last decades [1–3]. The 60° bond angles in P_4 seem to suggest a high strain energy [4,5] which should diminish for larger cages and thus favor their formation. However, despite the isolation of a substantial number of anionic P_n cages in the form of polyphosphide salts [6] or transition metal complexes [7], neutral P_n species have thus far eluded isolation despite mounting spectroscopic evidence for their formation [1].

Following the strain argument, the highly symmetric P_8-cubane **4** with its 90° bond angles (Fig. 1) seemed a particularly promising candidate for isolation. However, an early ab initio study by Fluck et al. predicted a *destabilization* of P_8 *vs.* 2 P_4 by no less than 47 kcal mol^{-1} [8]. Although a subsequent MNDO study by Bock et al. reached the exact opposite conclusion [9], subsequent increasingly sophisticated ab initio studies all confirmed the low stability of **4** [10,11] with 39 kcal mol^{-1} as the most recent destabilization energy vs. P_4 [11a]. Higher P_n species have been investigated more recently by Häser and Ahlrichs, but are also predicted to be thermodynamically unstable with respect to P_4 [11].

The surprisingly low stability of **4** vs P_4 has been attributed to a reduced lone pair repulsion in P_4 [10a]. This is in part due to the geometry of P_4 [10a] but also the result of the high s-character of the lone pairs in P_4 [12]. A second contributing factor seems to be the stabilization of P_4 through delocalized bonding [10e].

In 1992, the search for P_8 took an unexpected turn when Jones et al. gave computational evidence suggesting that the cuneane isomer of P_8 (**6**) (Fig. 1) is significantly more stable than **4** [10f,g] although

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Dedicated to Professor Dr. Alfred Schmidpeter on the occasion of his 75th birthday.

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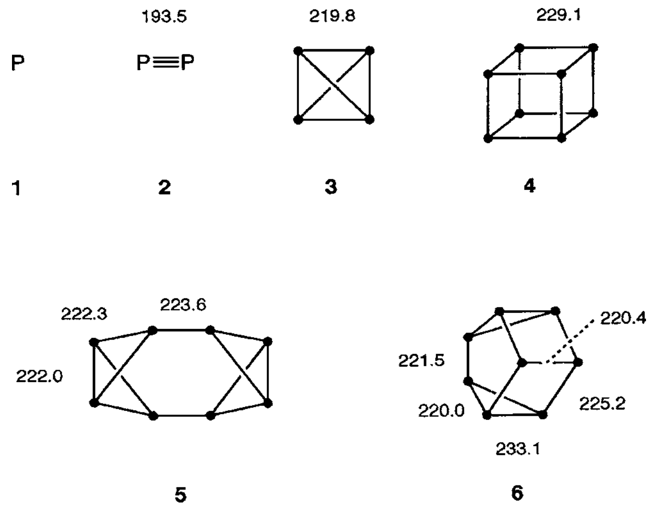

FIGURE 1 Selected P_n species with calculated P—P bond distances (in pm) at the MP2/6-31G(d′) level.

still less stable than P_4. A subsequent high level CCSD(T) study by Häser gave a numerical value of +6.0 kcal mol^{-1} (ΔE_o) for the formation of **6** from 2 P_4 [11e].

Despite the increasing level of sophistication, previous computational studies on the thermochemistry of P_n species have relied on single-method calculations [10,11] which are known to produce maximum errors of up to 10 kcal mol^{-1} [13]. In this study, we use the significantly more accurate compound calculation approach (CBS-Q method) to establish the relative energies of atomic phosphorus, P_2, P_4 (white phosphorus), P_8-cubane (**4**), and two isomeric P_8 cage structures (**5**,**6**).

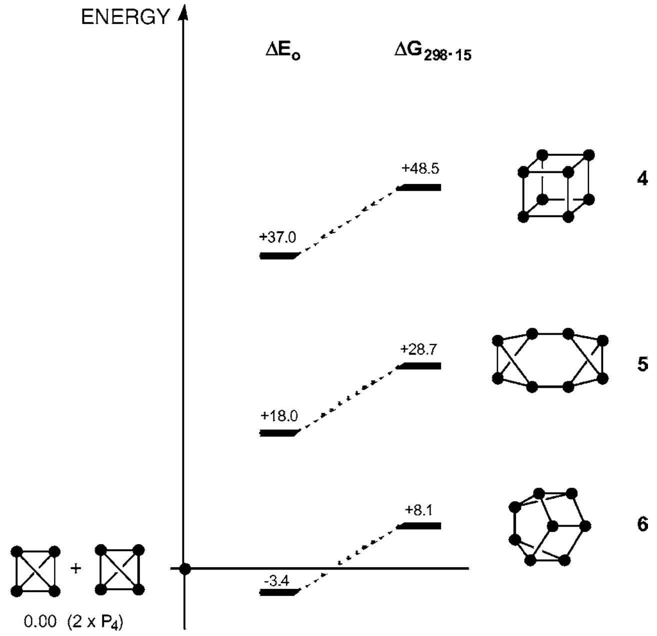

FIGURE 2 Energies ΔE_o and $\Delta G_{298.15}$ (in kcal mol^{-1}) of selected P_8 cage structures (**4**–**6**) vs. 2×P_4.

RESULTS AND DISCUSSION

Method

Computational methods that include electron–electron correlation have greatly reduced the error margins of thermochemical predictions, but the maximum absolute errors of 10 kcal mol^{-1} encountered in single-method calculations [13] are still large if compared with the error margin of most experimental data found in the literature [14].

The analysis of the systematic errors of single-method calculations has led to the development of multimethod approaches (“compound calculations”) like the CBS-Q [15] or G3 [16] methods. Both methods have error margins of only 1.5 kcal mol^{-1} [17] and are the state-of-the-art computational approach for the calculation of accurate thermochemical data [17,18]. Their use is currently limited to small molecules with typically up eight heavy atoms.

In this communication, we use the CBS-Q approach to establish reliable thermodynamic stabilities for P_8-cubane (**4**) and the isomers **5** and **6**. The experimental bond energy of P_2 and the experimental heat of formation of P_4 from P_2 are used as reference points to verify the accuracy of the CBS-Q method for P_n cages.

The calculations were carried out with the Gaussian 03 M suite of programs, Rev. B.05, [19] energies were converted using the factor 1 hartree = 627.51 kcal mol^{-1}. All optimized structures are verified as local minima through frequency calculations. The lowest frequencies ω_o of the respective structures and their energies E_o, $E_{298.15}$, $H_{298.15}$, and $G_{298.15}$ are listed in Table 1, bond distances are shown in Fig. 1.

Optimized Structures

The structures are optimized at the MP2/6-31G(d′) level and obtained from the third step of the six-step CBS-Q procedure. The bond angles in the examined P_n-cages are largely defined by the geometry of the respective cages and assume the expected values.

Experimental bond distances for white phosphorus range from 221 to 222 pm [21], and the MP2/6-31G(d′) bond distance of pm 219.8 is thus slightly shorter than the smallest experimental value. This deviation has been noted previously for other levels of theory by Häser [11e] and is not an artifact of the comparatively small 6-31G(d′) basis set or the MP2 method but is observed with large basis set sets and other methods as well [22].

TABLE 1 Energies (in hartrees), Lowest vibrational Frequencies ω_o (in cm^{-1}), and P—P Bond Distances (in pm) of Selected P_n Species at the CBS-Q Level of Theory

	E_o	$\Delta E_{298.15}$	$\Delta H_{298.15}$	$\Delta G_{298.15}$	*Point Group*	ω_o	*P—P*
^2P	−340.758921	−340.757505	−340.756560	−340.774426	–	–	–
^4P	−340.816941	−340.815525	−340.814580	−340.833101	–	–	–
^6P	−340.359381	−340.357965	−340.357021	−340.375924	–	–	–
P_2	−681.818225	−681.815795	−681.814851	−681.839548	$D_{\infty h}$	908	193.46
P_4	−1363.726615	−1363.722249	−1363.721304	−1363.752920	T_d	407	219.78
P_8(**4**)	−2727.394266	−2727.384971	−2727.384027	−2727.428572	C_2	167	228.87
P_8(**5**)	−2727.424516	−2727.414790	−2727.413846	−2727.460170	C_{2v}	80	221.96 222.27 223.60
P_8(**6**)	−2727.458622	−2727.449357	−2727.448413	−2727.492928	C_2	173	220.38 221.47 219.96 225.16 233.08

Excited states of phosphorus (^2P, ^6P) included for comparison only.

The calculated phosphorus–phosphorus bond distances for the P_8 cages **4–6** show some interesting trends. The bond distance of 219.8 pm in P_4 (**3**) marks the short end of the range; the maximum value of 233.1 pm is obtained for **6**. The remaining bond distances in **6** and those in **5** are very similar and closely resemble the average P–P distances of 222 pm found in Hittorf's violet phosphorus and black phosphorus (223 pm) [23]. The bond distance in **4** (229 pm) appears significantly elongated which correlates well with the high energy of **4** (see below).

Energies

The experimental bond energy of P_2 corresponding to the dissociation of P_2 into two phosphorus atoms in their quartet ground state ($[Ne]s^2P^3$) is difficult to reproduce even with advanced single-method calculations like the CCSD(T) method [11e], and is also known to show a poor basis-set convergence [11e]. Notwithstanding these difficulties, the calculated CBS-Q bond energy (E_o) of +115.7 kcal mol^{-1} is in excellent agreement with the experimental value of +116 kcal mol^{-1} [24].

The experimental value for the dimerization energy of P_2 to P_4 (−5 kcal mol^{-1}) [25] is reproduced with similar accuracy (−56.6 kcal mol^{-1}). In view of these results and the generally known high accuracy of the CBS-Q method, the approach seems well suited to establish reliable thermodynamic stabilities for the P_8 cage structures **4–6**.

The formation of P_8-cubane (**4**) from P_4 is confirmed to be strongly endothermic with a ΔE_o value of +37.0 kcal mol^{-1} and is further disfavored entropically with $T\Delta S^o$ amounting to +11.7 kcal mol^{-1} at standard temperature (298.15 K). The free energy ΔG^o for the formation of **4** from white phosphorus thus amounts to +48.5 kcal mol^{-1}. The entropic factors for the formation of the isomeric P_8 cages **5** and **6** are nearly identical so that the relative stabilities of the P_8-cage structures **4–6** will be largely independent from T (compare Table 2), while their dissociation into P_4, P_2, or atomic phosphorus will be strongly favored by an increase in temperature.

TABLE 2 Reaction Energies (in kcal mol^{-1}) for the Interconversion of Selected P_n Species at the CBS-Q Level of Theory. Selected ab initio energies from previous single method studies are given in parentheses.

Reaction	E_o	$\Delta E_{298.15}$	$\Delta H_{298.15}$	$T\Delta S_{298.15}$	$\Delta G_{298.15}$
$2\,{}^4P \rightarrow P_2$	−115.7 (−104.5)[a]	−115.9	−116.5	+7.7	−108.8
$2P_2 \rightarrow P_4$	−56.6 (−56.7)[a]	−56.9	−57.5	+11.2	−46.3
$2P_4 \rightarrow$ **4**	+37.0 (+56.6)[b]	+37.3	+36.8	+11.7	+48.5
$2P_4 \rightarrow$ **5**	+18.0 (+24.1)[b]	+18.6	+18.1	+10.6	+28.7
$2P_4 \rightarrow$ **6**	−3.4 (+10.0)[b]	−3.1 (+6.0)[c]	−3.6	+11.7	+8.1

[a] Raghavachari et al. (1985), MP4/6-31G(2df) level [10c].

[b] Häser et al. (1992), MP2/SVP level [11a].

[c] Häser et al. (1995), CCSD(T)fc/SVP//MP2/SVP level [11e].

The CBS-Q energies calculated for the structures **4–6** significantly revise the values obtained by previous high-level computational studies. A comparison shows that the single-method calculations underestimate the stability of **4–6** vs. 2 P_4 by 6–20 kcal mol^{-1}.

Average P—P bond energies E_o for P_4 (**3**, 48.0 kcal mol^{-1}), cubic P_8 (**4**, 44.9 kcal mol^{-1}), **5** (46.5), and **6** (48.3 kcal mol^{-1}) can be obtained by dividing the atomization energies of **3–6** by the number of bonds. While the differences appear small, they nevertheless add up to significant energy differences due the large number of P—P bonds present in the cages.

The thermodynamic data of the investigated P_8 species do not allow the prediction of their kinetic stability toward decomposition or their rate of formation. However, the fact that the cuneane cage **6** is predicted to be thermodynamically more stable than P_4 at low temperatures is nevertheless remarkable and bodes well for future attempts to isolate **6** under low-temperature matrix conditions. While the direct formation of P_8 cages from phosphorus atoms or P_2 molecules is a highly unlikely process, successive cage expansion reactions with reactive phosphorus sources like atomic phosphorus or P_2 are a viable alternative.

CONCLUSION

The predictions of older ab initio calculations that cubic P_8 (**4**) is destabilized vs. P_8-cage structures of lower symmetry are confirmed through high precision CBS-Q calculations. P_8-cuneane (**6**), the most stable P_8 isomer investigated in this study is found to be *lower* in energy than $2\times P_4$ at $T = 0$ K ($\Delta E_o - 3.37$ kcal mol^{-1}) but disfavored at higher temperatures for entropic reasons ($\Delta G_{298.15} + 8.10$ kcal mol^{-1}).

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