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Thermochemistry of phosphorus sulfide cages: An extreme challenge for high-level ab initio methods

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ABSTRACT

The enthalpies of formation and isomerization energies of P_4S_n molecular cages are not experimentally (or theoretically) well known. We obtain accurate enthalpies of formation and isomerization energies for P_4S_n cages (n = 3, 4, 5, 6, and 10) by means of explicitly correlated high-level thermochemical procedures approximating the CCSD(T) and CCSDT(Q) energies at the complete basis set (CBS) limit. The atomization reactions have very significant contribution from post-CCSD(T) correlation effects and, due to the presence of many second-row atoms, the CCSD and (T) correlation energies converge exceedingly slowly with the size of the one-particle basis set. As a result, these cage structures are challenging targets for thermochemical procedures approximating the CCSD(T) energy (e.g., W1-F12 and G4). Our best enthalpies of formation at 298 K ($\Delta f H^{0}_{298}$) are obtained from thermochemical cycles in which the P₄S_n cages are broken down into P₂S₂ and S₂ fragments for which highly accurate $\Delta_{f}H^{o}_{298}$ values are available from W4 theory. For the smaller P₄S₃ and P₄S₄ cages the reaction energies are calculated at the CCSDT(Q)/CBS level and for the larger P4S5, P4S6, and P4S10 cages they are obtained at the CCSD(T)/CBS level. Our best $\Delta f H^{\circ}_{298}$ values are -94.5 (P4S₃), -108.4 (α -P4S₄), -98.7 (β -P4S₄), -126.2 (α -P4S₅), -126.1 (β -P4S₅), -112.7 (γ -P4S₅), -144.7 (α -P4S₆), -153.9 (β -P4S₆), -134.4 (γ -P4S6), -136.3 (δ -P4S6), -118.7 (ϵ -P4S6), and -215.4 (P4S10) kJ mol⁻¹. Interestingly, we find a linear correlation ($R^2 = 0.992$) between the enthalpies of formation of the most stable isomers of each molecular formula and the number of atoms in the P₄S_n cages. We use our best $\Delta t H^{o}_{298}$

values to assess the performance of a number of lower-cost composite ab initio methods. For absolute enthalpies of formation, G4(MP2) and G3(MP2)B3 result in the best overall performance with root-mean-square deviations (RMSDs) of 10.6 and 12.9 kJ mol⁻¹, respectively, whereas G3, G3B3, and CBS-QB3 result in the worst performance with RMSDs of 27.0–38.8 kJ mol⁻¹. In contrast to absolute enthalpies of formations, all of the considered composite procedures give a good-to-excellent performance for the isomerization energies with RMSDs below the 5 kJ mol⁻¹ mark.

Keywords: Phosphorus sulfide cages, Thermochemistry, CCSD(T), CCSDT(Q), G4 theory.

1. Introduction

The reaction between the elements phosphorus and sulfur to give phosphorus sulfides was first observed over 250 years ago by Marggraf.¹ Over the century that followed, the discoveries of no less than 14 individual phosphorus sulfide compounds were reported.² However, disagreement in the literature regarding the existence of those compounds, ranging in their molecular structure from P₄S to P₂S₁₂, as distinct new compounds or mere mixtures persisted.^{2,3} Bringing clarity into what he described as a "Komödie der Irrungen" (comedy of errors),² Stock through a series of communications concluded that only P₄S₃, P₄S₇ and P₄S₁₀ could be considered individual compounds with certainty.^{2,4,5,6,7} Later this collection was extended to include the notably less stable P₄S₅, P₄S₆, P₄S₈ and P₄S₉.^{8,9}

After this narrowing of the field, the more recent research focus in the subject area has been on the unusual cage-like structures of the phosphorus sulfides and ³¹P NMR and X-ray diffraction studies have allowed for numerous structural isomers to be identified.^{3,9,10,11,12,13,14,15}

The majority of the known isomers of the form P_4S_n can be produced in complex mixtures from the oxidation of phosphorus by sulfur at temperatures below 100° C.¹⁶ It has been hypothesised that under such conditions an initial reactive P_4S_8 intermediate including a P_4 cage

and a cyclic S₈ structure is formed. After ring-opening of S₈ a resulting diradical intermediate is then proposed to undergo a cascade of reactions in which the sulfur atoms are incorporated into the P₄ cage structure.¹⁷ Specific synthesis methods for individual isomers are, however, available and have been summarised by Blachnik and Hoppe.¹⁸

Another focus area in the research on phosphorus sulfides has been their reactivity, in particular with respect to P₄S₁₀.¹⁹ Since its first discovery by Berzelius in 1843²⁰ from the highly exothermic reaction of white phosphorus with sulfur, P₄S₁₀ has found numerous commercial applications in the productions of insecticides as well as additives for lubricants, oil flotation agents, plasticizers and flame retardants.^{9,19} It was further identified as a useful thionating agent for organic as well as inorganic compounds and has been applied in the synthesis of a number of heterocycles such as thiazoles and thiophenes.¹⁹

The experimental determination of thermodynamic properties of phosphorus sulfides has proven much more elusive and is complicated by the existence of numerous isomers and low melting points.²¹ A small number of studies largely from the middle of the 1900s nevertheless provide some approximate reference experimental data. However, significant variation is observed between reported enthalpies of formation for phosporus sulfides. From direct reaction calorimetry and benzoic acid solution calorimetry with amorphous red phosphorus (I) and orthorhombic α -sulfur as references, Cueilleron and Vincent^{21,22,23} reported enthalpies of formation ($\Delta t H^2_{298}$) of –154.4, –235.1, and –228.0 kJ mol⁻¹ for P4S₃, P4S₅, and P4S₁₀, respectively. In contrast to this Treadwell and Beeli²⁴ report an enthalpy of formation of –123.0 kJ for P4S₃ from elemental red phosphorus and sulfur (it is unclear precisely which allotropes were used as references) whereas Hartley *et al.*²⁵ arrive at a value of approximately –134 kJ mol⁻¹. Variations are likely due to different reference allotropes being used and it is unclear which isomers of the

more sulfur-rich compounds were present in the study by Cueilleron and Vincent.^{21,22,23}

Computational investigations on phosphorus sulfides are scarce. Ystenes *et al.*^{26,27} calculated the geometries and vibrational frequencies for $P_4S_3^{26}$ and α -P₄S₄ at the Hartree–Fock level.²⁷ Jones and Seifert carried out molecular dynamics and low-level density functional theory (DFT) calculations to explore the structural parameters and bond energies of several isomers of P₄S₃ and P₂S₅.^{28,29} More accurate ab initio calculations (up to CCSD(T)) were carried out by Császár to examine the energies and structural parameters of the smaller P₂S₂ isomers.³⁰

In light of the lack of experimental thermochemical data for individual phosphorus sulfide isomers and the complications associated with accurate experimental determination of such values, high-accuracy computational data can serve as valuable reference data. In this study we use the Wn-F12 (n = 1-3) methods to determine accurate thermochemical data for the different known isomers of P4S₃, P4S₄, P4S₅, P4S₆, and P4S₁₀. The Wn-F12 theories are high-level composite ab initio procedures for the calculation of the all-electron, relativistic energies at the CCSD(T)/CBS (W1-F12 and W2-F12) and CCSDT(Q)/CBS (W3lite-F12) limits.^{31,32} W1-F12 and W2-F12 theories can achieve an accuracy in the sub-kcal mol⁻¹ range for enthalpies of formation of molecules whose wavefunctions are dominated by dynamical correlation, whilst W3lite-F12 theory achieves kJ mol⁻¹ accuracy for such enthalpies of formation.^{31,32,33,34,35} Using our high-level thermochemical data we find that molecular cages containing second-row atoms entail challenges for ab initio methods and we examine strategies for overcoming these challenges. Our results suggest that the available experimental enthalpies of formation should be revised by appreciable amounts. Finally, our benchmark thermochemical values allow us to evaluate the performance of a number of lower-cost Gn and CBS thermochemical procedures.

Figure 1 shows the set of P_4S_n molecular cages considered in this study. This set comprises the experimentally reported isomers of the molecular formulas P_4S_n (n = 3, 4, 5, and 6) as well as the well-known Berzelius reagent P_4S_{10} .^{16,36} It is worth noting that different naming conventions are used in the literature on phosphorus sulfides. Here, we use the most prevalent nomenclature which adds a Greek letter prefix to those P_4S_n isomers for which more than one isomer is possible. These prefixes advance through the alphabet in the order in which the isomers were discovered experimentally.



Figure 1. B3LYP-D3/Def2-TZVPP optimized structures for experimentally known P_4S_n structures. Atomic color scheme: P, orange; S, yellow.

2. Computational details

In order to obtain accurate thermochemical properties for the P_4S_n isomers, calculations were carried out using the high-level ab initio Wn-F12 procedures. Wn-F12 theories combine explicitly correlated F12 techniques³⁷ with basis-set extrapolations in order to approximate the CCSD(T) (coupled cluster with single, double, and quasiperturbative triple excitations) and CCSDT(Q) (coupled cluster with single, double, triple, and quasiperturbative quadruple excitations) basis-set-limit energies. The following gives a brief overview of the various steps in Wn-F12 theories. (For further details see refs. 31, 33, and 38.) In W1-F12, the Hartree–Fock and valence CCSD-F12 correlation energy components are extrapolated from the VDZ-F12 and VTZ-F12 basis sets, where VnZ-F12 denotes the cc-pVnZ-F12 basis sets of Peterson *et al.*³⁹ The complementary auxiliary basis set (CABS) singles correction is included in the SCF energy.^{40,41,42} The (T) valence correlation energy is obtained from the original W1,⁴³ i.e., it is extrapolated from the AVDZ and AVTZ basis sets.^{44,45} The diagonal, fixed-amplitude 3C(FIX) ansatz,^{41,46,47,48} and the CCSD-F12b approximation are used in all of the explicitly correlated coupled cluster calculations.^{42,49} The CCSD inner-shell contribution is calculated with the core-valence weighted correlation-consistent cc-pwCVTZ basis set of Peterson and Dunning,⁵⁰ 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)^{51,52} is obtained as the difference between non-relativistic CCSD(T)/AVDZ and relativistic CCSD(T)/AVDZ-DK calculations.53 The diagonal Born–Oppenheimer corrections are calculated at the HF/cc-pVTZ level of theory using the CFOUR program suite.⁵⁴ In W2-F12 the HF, valence CCSD, valence (T), core-valence. and scalar relativistic components are obtained from larger basis sets.³¹ W3lite-F12 theory

additionally includes post-CCSD(T) contributions up to CCSDT(Q). Specifically, the higherorder connected triples (CCSDT–CCSD(T)) valence correlation contribution is calculated using the cc-pVDZ and cc-pVTZ(no f 1d) basis sets, where cc-pVTZ(no f 1d) indicates the combination of the sp part of the cc-pVTZ basis set combined with the d function from the ccpVDZ basis set.³² The (Q) contribution is calculated with the cc-pVDZ basis set. All the CCSD(T) calculations were carried out with the Molpro 2012.1 program suite⁵⁵ whilst the post-CCSD(T) calculations were carried out with MRCC.⁵⁶

Geometries of all structures were optimized at the B3LYP-D3/Def2-TZVPP level of theory.^{57,58,59,60,61} Empirical D3 dispersion corrections^{62,63} are included using the Becke–Johnson⁶⁴ damping potential as recommended in ref. 60. To evaluate the quality of our DFT geometries, we optimized the geometry of P₄S₃ at the CCSD(T)/cc-pV(Q+d)Z level of theory. We find that the differences in the P–S and P–P bond lengths between the two structures are equal to or smaller than 0.01 Å (for further details see Figure S1 of the Supporting Information). Figure S2 of the Supporting Information lists the B3LYP-D3/Def2-TZVPP bond lengths of the structures in Figure 1. The lengths of the P–S and P–P bonds span fairly narrow ranges. In particular, the lengths of the (i) endocyclic P–S bonds range between 2.071–2.176 Å, (ii) endocyclic P–P bonds range between 2.254–2.427 Å, and (iii) exocyclic P–S bonds range between 1.918–1.922 Å.

Harmonic vibrational frequency analyses were performed at the B3LYP-D3/Def2-TZVPP level of theory to confirm that all stationary points are equilibrium structures (i.e., all structures were confirmed to have all real frequencies). Zero-point vibrational energies (ZPVEs) and enthalpic corrections were obtained from these calculations. The ZPVEs were scaled by 0.99 as recommended in refs. 65 and 66. All geometry optimizations and frequency calculations were performed using the Gaussian 09 program suite.⁶⁷

In addition, the performance of more approximate Gaussian-*n*⁶⁸ and CBS-type⁶⁹ composite thermochemical procedures is assessed.^{33,70,71} We consider the following composite procedures: G4,⁷² G4(MP2),⁷³ G4(MP2)-6X,⁷⁴ G3,⁷⁵ G3(MP2),⁷⁶ G3B3,⁷⁷ G3(MP2)B3,⁷⁷ and CBS-QB3.^{78,79}

3. Results and discussion

3.1. Multireference considerations. We begin by assessing the contributions from post-CCSD(T) excitations for the P₄S_n (n = 3-10) systems. The percentage of the total atomization energy (TAE) accounted for by the quasiperturbative triple excitations, %TAE[(T)],^{33,80,81,82} has been shown to be a reliable energy-based diagnostic for the importance of post-CCSD(T) contributions to the total atomization energies. %TAE[(T)] values between 5–10% indicate that post-CCSD(T) contributions should normally range between 2–8 kJ mol^{-1,33} Table S1 of the Supporting Information gathers the %TAE[(T)] values for the P₄S_n (n = 3-10) systems. The %TAE_e[(T)] values for these species lie in a narrow range of 6.6–6.9%. This suggests that the considered species are dominated by moderate non-dynamical correlation effects, and that post-CCSD(T) contributions to the total atomization energies should normally not exceed the ~8 kJ mol⁻¹ mark.

3.2. CCSD(T)/CBS and CCSDT(Q)/CBS enthalpies of formation for the smaller P₄S₃ and P₄S₄ isomers via atomization reactions. Table 2 gives the component breakdown of the W1-F12 and W2-F12 (CCSD(T)/CBS) and W3lite-F12 (CCSDT(Q)/CBS) atomization energies as

well as the final enthalpies of formation at 0 K ($\Delta_f H^{\circ}_0$) and 298 K ($\Delta_f H^{\circ}_{298}$) for P₄S₃ and two P₄S₄ isomers. The magnitude of the HF component of the TAE (Δ HF) is very large, reaching up to

1241.1 kJ mol⁻¹ for β -P₄S₄ at the W2-F12 level. Remarkably, the HF components from W1-F12 theory differ by ±0.4 kJ mol⁻¹ from the W2-F12 values, indicating that the latter should be fairly close to the basis-set limit. This is consistent with results obtained for first-row cage structures (e.g., tetrahedrane, triprismane, and cubane), for which the Δ HF component from W1-F12 theory is less than 0.4 kJ mol⁻¹ away from results obtained at the HF/VQZ-F12 level of theory.¹⁰⁵

The valence CCSD correlation contribution (Δ CCSD-F12) to the TAE is similar to the HF component, i.e., it increases the TAE by about 1000 kJ mol⁻¹. However, the basis set convergence of the CCSD component is much slower than that of the HF component. In particular, the W1-F12 values systematically underestimate the W2-F12 CBS values by 15.5 (P4S₃), 18.2 (α -P4S₄), and 18.5 (β -P4S₄) kJ mol⁻¹. The valence (T) correlation contribution (Δ (T), Table 1) ranges between 157.1 (P4S₃) and 176.7 (α -P4S₄) kJ mol⁻¹. Again, the W1-F12 values underestimate the W2-F12 values by chemically significant amounts of 6.4 (P4S₃) and 7.2 (α -P4S₄ and β -P4S₄) kJ mol⁻¹.

The core–valence (Δ CV) correlation contributions are still relatively large reaching up to 12.9 kJ mol⁻¹ for α -P₄S₄. The scalar relativistic (Δ Rel) and first-order spin-orbit coupling (Δ SO) contributions both reduce the atomization energies by up to ~10 kJ mol⁻¹.

<i>c</i> 1									
Compound	P ₄ S ₃	$\alpha - P_4S_4$	β-P4S4	P ₄ S ₃	$\alpha - P_4S_4$	β-P ₄ S ₄	P ₄ S ₃	$\alpha - P_4S_4$	β-P ₄ S ₄
	CCSD(T)/CB	S					CCSDT(Q)/	CBS	
	W1-F12			W2-F12			W3lite-F12		
ΔHF	1078.1	1232.9	1240.7	1078.4	1233.3	1241.1	g	g	g
ΔCCSD	959.8	1077.2	1063.8	975.3	1095.4	1082.3	g	g	g
Δ (T)	150.7	169.5	165.1	157.1	176.7	172.3	g	g	g
ΔT	N/A	N/A	N/A	N/A	N/A	N/A	-7.1	-7.2	-6.3
(Q)	N/A	N/A	N/A	N/A	N/A	N/A	12.6	13.9	13.5
$\Delta \mathbf{CV}$	10.5	11.2	11.1	11.9	12.9	12.8	g	g	g
Δ Rel	-8.6	-9.6	-10.0	-7.0	-7.8	-8.2	g	g	g
ΔSO	-7.0	-9.4	-9.4	f	f	f	f	f	f
Δ DBOC	0.1	0.1	0.1	f	f	f	f	f	f
TAEe ^{a,h}	2183.7	2471.9	2461.4	2208.9	2501.2	2491.0	2214.4	2507.9	2498.2
$\Delta \mathbf{ZPVE}^{b}$	31.9	36.8	36.4	f	f	f	f	f	f
TAE ₀ ^{c,i}	2151.7±10.4	2435.2±10.4	2425.0±10.4	2176.9±7.7	2464.4±7.7	2454.5±7.7	2182.4±6.4	2471.1±6.4	2461.7±6.4
Δ f H^{0} 0 ^{<i>d,i</i>}	-62.7	-71.2	-61.0	-87.9	-100.5	-90.6	-93.4	-107.2	-97.8
Δ f H^{0} 298 e,i	-73.1	-82.4	-71.9	-98.4	-111.6	-101.4	-103.9	-118.3	-108.6

Table 1. Component breakdown of the W1-F12, W2-F12, and W3-F12lite atomization energies

for P_4S_3 and two P_4S_4 isomers and predicted theoretical enthalpies of formation (kJ mol⁻¹).

^gVibrationless, relativistic, all-electron TAEs. ^hZPVE correction from B3LYP-D3/Def2-TZVPP harmonic frequencies (scaled by 0.99, see also ref. 65). ⁱZPVE-inclusive, relativistic, all-electron TAEs. ^jEnthalpies of formation at 0 K obtained using the following atomic enthalpies of formation at 0 K: $\Delta t H^{\circ}(P) = 316.06\pm0.4$ (ref. 85), $\Delta t H^{\circ}(S) = 274.93\pm0.15$ (CODATA).⁸⁶ ^kEnthalpies of formation at 298 K obtained using enthalpy functions, $H_{298}-H_{0}$, from CODATA 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. ^fTaken from W1-F12 theory. ^gTaken from W2-F12 theory. ^hUncertainties on the TAE₀ values correspond to 95% confidence intervals estimated as twice the RMSDs taken from ref. 31 (i.e., ±6.2 for W1-F12, ±3.5 for W2-F12, and ±2.6 kJ mol⁻¹ for W3-F12), in addition, to account for potential issues with the post-CCSD(T) treatment in W3lite-F12 and the scaled harmonic ZPVEs a conservative uncertainty of 1 kcal mol⁻¹ is added.

As discussed in the above paragraph the W1-F12 \triangle CCSD and \triangle (T) values underestimate

the W2-F12 values by significant amounts. As a result, the W1-F12 TAEs underestimate the W2-

F12 values by staggering amounts of 25.2 (P4S₃), 29.3 (α -P4S₄), and 29.6 (β -P4S₄) kJ mol⁻¹. Thus,

it is clear that the phosphorus sulfide cages pose a significant challenge for CCSD(T)/CBS

methods such as W1-F12. In Section 3.6 we will evaluate the performance of even more approximate CCSD(T)/CBS methods such as G4, G4(MP2), and CBS-QB3 for these systems.

What about post-CCSD(T) contributions to the TAEs? We were able to obtain the T–(T) (ΔT) component from W3lite theory, ³² in which it is extrapolated from the cc-pVDZ and ccpVDZ(4s3p1d) basis sets. We note, however, that it has been found that extrapolating the T-(T) component from these fairly small basis sets may fall short for systems containing many secondrow atoms.^{32,80,83} Unfortunately, the CCSDT/cc-pVTZ calculations, involving 11 and 26 billion amplitudes for the P₄S₃ and P₄S₄ systems, respectively, are prohibitively expensive with current mainstream technology. On the other hand, the CCSDT/cc-pVDZ(4s3p1d) calculations involve about 2 and 4 billion amplitudes, respectively and are feasible for these systems. The T-(T)component extrapolated from the cc-pVDZ and cc-pVDZ(4s3p1d) basis sets as prescribed in W3.2lite theory reduces the TAEs by 7.1 (P4S₃), 7.2 (α -P4S₄), and 6.3 (β -P4S₄) kJ mol⁻¹. The quasiperturbative connected quadruple excitations ((Q)/cc-pVDZ) component increases the TAEs by 12.6 (P₄S₃), 13.9 (α -P₄S₄), and 13.5 (β -P₄S₄) kJ mol⁻¹. Overall, our estimated post-CCSD(T) contributions increase the TAEs by 5.5 (P₄S₃), 6.7 (α -P₄S₄), and 7.2 (β -P₄S₄) kJ mol⁻¹. These results are consistent with the %TAE[(T)] diagnostic which predicted that the post-CCSD(T) contributions should not exceed the ~ 8 kJ mol⁻¹ mark (Section 3.1).

Summing up our Δ HF, Δ CCSD-F12, Δ (T), Δ T, Δ (Q), Δ CV, Δ Rel, Δ SO, Δ DBOC, and Δ ZPVE contributions to the TAEs (Table 1), we obtain TAEs at 0 K (TAE₀) of: 2182.4±6.4 (P₄S₃), 2471.1±6.4 (α -P₄S₄), and 2461.7±6.4 (β -P₄S₄) kJ mol⁻¹. As recommended in ref. 84, 95% confidence intervals for the TAE₀ values are estimated as twice the RMSDs reported in ref. 31. In addition, a conservative uncertainty of 1 kcal mol⁻¹ is added to account for potential issues with the post-CCSD(T) treatment in W3lite-F12 and scaled harmonic ZPVEs. We convert the TAEs to

enthalpies of formation at 0 K using a semi-experimental atomic enthalpy of formation for P obtained from highly accurate W4 calculations^{80,85} and a CODATA atomic enthalpy of formation at 0 K for S.⁸⁶ Our Δ*tH*^o₀ values are: -93.4 (P4S₃), -107.2 (α-P4S₄), and -97.8 (β-P4S₄) kJ mol⁻¹. These Δ*tH*^o₀ values are converted to enthalpies of formation at 298 K (Δ*tH*^o₂₉₈) using the CODATA⁸⁶ enthalpy functions (H₂₉₈-H₀) for the elemental reference states and molecular enthalpy functions, which are obtained within the rigid-rotor harmonic oscillator approximation from the B3LYP-D3/Def2-TZVPP geometries and harmonic frequencies. Our Δ*tH*^o₂₉₈ values are: -103.9 (P4S₃), -118.3 (α-P4S₄), and -108.6 (β-P4S₄) kJ mol⁻¹. Our enthalpy of formation for P4S₃ is significantly higher than the experimental values of -123.0,²⁴ -134,²⁵ and -154.4 kJ mol⁻¹ (taken from ref. 21).

3.3. CCSD(T)/CBS and CCSDT(Q)/CBS enthalpies of formation of P₄S₃ and P₄S₄ isomers via thermochemical cycles. The results of the previous section show that W1-F12 theory underestimates our CCSDT(Q)/CBS TAEs by amounts ranging from 25.2 (P₄S₃) to 29.6 (β -P₄S₄) kJ mol⁻¹, and even W2-F12 theory still underestimates them by 5.5–7.2 kJ mol⁻¹. One way of improving thermochemical predictions of approximate theoretical methods is to use thermochemical cycles in which the target molecule is broken down into smaller fragments for which accurate enthalpies of formation are available from theory or experiment. It has been shown in numerous investigations that the accuracy of this approach improves as the chemical environments on the two sides of the chosen reaction are conserved to higher degrees.^{87,88,89,90,91,92,93,94,95,96,97,98,99,100,101,102,103,104,105} This is due to an increasing degree of error cancellation between reactants and products. Nevertheless, an essential requirement of this approach is that precisely known enthalpies of formation are available for all the fragments involved in the reaction. Possible fragment molecules, for which highly accurate enthalpies of formation are available from W4 theory, are: P₂, S₂, PS, S₃, S₄ P₂S₂, and P₄ (shown in Figure 2). It should be pointed out that W4 theory, which approximates the all-electron, relativistic, DBOC-inclusive CCSDTQ5/CBS limit energy has been found to give RMSDs and mean absolute deviations (MADs) of 0.36 and 0.27^{33,34} relative to highly accurate experimental TAEs obtained from the Active Thermochemical Tables (ATcT) network of Ruscic and co-workers.¹⁰⁶ These error statistics imply sub-kJ mol⁻¹ 95% (2 σ) confidence intervals of ±0.7 kJ mol⁻¹ and 99% (3 σ) confidence intervals of about 1 kJ mol⁻¹. Table 2 gathers the W4 enthalpies of formation at 298 K for the fragment species.



Figure 2. CCSD(T)/cc-pV(Q+d)Z optimized structures for selected fragments into which the P₄S_n species are broken in reactions 1–12.

	Δ f H^{o} 298
S_2	124.5
S ₃	137.4
S_4	143.2
\mathbf{P}_2	144.9
\mathbf{P}_4	60.5
PS	159.9
P_2S_2	57.9

Table 2. Enthalpies of formation at 298 K ($\Delta_t H^{\circ}_{298}$) obtained from W4 theory for the small species involved in reactions 1–12 (kJ mol⁻¹).

In the present work we will consider the following nine thermochemical cycles for obtaining the enthalpies of formation of the P_4S_n species:

$P_4S_n \rightarrow 2 P_2 + n/2 S_2 (n = 3, 4)$	(1)
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$$P_4S_n \rightarrow 2 P_2 + n/3 S_3 (n = 3, 4)$$
 (2)

$$P_4S_n \rightarrow 2 P_2 + n/4 S_4 \ (n = 3, 4)$$
 (3)

$$P_4S_n \to P_4 + n/2 S_2 \ (n = 3, 4)$$
 (4)

$$P_4S_n \to P_4 + n/3 S_3 \ (n = 3, 4)$$
 (5)

$$P_4S_n \to P_4 + n/4 S_4 \ (n = 3, 4)$$
 (6)

$$P_4S_n + (4 - n)/2 S_2 \rightarrow 2 P_2S_2 (n = 3, 4)$$
 (7)

$$P_4S_n + (4 - n)/3 S_3 → 2 P_2S_2 (n = 3)$$
 (8)

$$P_4S_n + (4 - n)/4 S_4 \rightarrow 2 P_2S_2 (n = 3)$$
 (9)

Table 3 gathers the enthalpies of formation at 298 K for the P4S3 and P4S4 species obtained from reactions 1-9. Let us start with the enthalpy of formation for P_4S_3 . Calculating the reaction energy at the CCSDT(Q)/CBS level (via W3lite-F12 theory), results in predicted enthalpies of formation ranging from -92.4 (reaction 6) to -97.2 (reaction 4) kJ mol⁻¹ when excluding reactions 1 and 2 which conserve the chemical environments on the two sides of the reaction to lesser extents. The average enthalpy of formation from reactions 3–9 is –95.3 kJ mol⁻¹. It is noteworthy that this ballpark figure is appreciably higher than the W3lite-F12 value predicted from the atomization reaction ($\Delta f H^{\circ}_{298} = -103.9 \text{ kJ mol}^{-1}$, Table 1). This indicates that even the high-level W3lite-F12 composite method is not sufficiently accurate for obtaining the enthalpy of formation of P₄S₃ via an atomization reaction. It is likely that one would have to go all the way to W4 theory for obtaining an accurate enthalpy of formation for P₄S₃ via an atomization reaction. However, these calculations are not feasible with current mainstream technology. The $\Delta t H^{0}_{298}$ values predicted from reactions 1 and 2, which break P₄S₃ into small fragments (P₂, S₂, and S_3) are sandwiched between the two limits. This suggests that reactions in which P_4S_3 is broken down into atoms or small fragments tend to overestimate the thermodynamic stability of the caged structure.

Compound	Reac.	W1-F12	W2-F12	W3lite-F12
P4S3	(1)	-95.9	-106.3	-101.4
	(2)	-102.4	-109.0	-100.1
	(3)	-110.1	-112.6	-96.7
	(4)	-90.6	-98.6	-97.2
	(5)	-97.2	-101.3	-95.8
	(6)	-104.8	-104.9	-92.4
	(7)	-93.8	-95.3	-94.5
	(8)	-91.6	-94.4	-94.9
	(9)	-90.8	-93.9	-95.5
α -P4S4 (D2d)	(1)	-107.5	-120.2	-115.4
	(2)	-116.3	-123.7	-113.6
	(3)	-126.5	-128.5	-109.1
	(4)	-102.3	-112.5	-111.1
	(5)	-111.0	-116.0	-109.4
	(6)	-121.2	-120.8	-104.8
	(7)	-105.4	-109.1	-108.4
β -P ₄ S ₄ (C _s)	(1)	-97.0	-110.0	-105.7
	(2)	-105.8	-113.6	-104.0
	(3)	-116.0	-118.4	-99.4
	(4)	-91.8	-102.3	-101.4
	(5)	-100.5	-105.9	-99.7
	(6)	-110.8	-110.7	-95.1
	(7)	-95.0	-99.0	-98.7

Table 3. W*n*-F12 enthalpies of formation at 298 K ($\Delta_t H^{\circ}_{298}$) obtained from reactions 1–9 for P₄S₃ and P₄S₄ isomers (kJ mol⁻¹).

The question that naturally arises is which of the reactions (3–9) gives the best enthalpy of formation for P₄S₃? One way to tackle this question is to look for a reaction that predicts fairly converged $\Delta_t H^{o}_{298}$ values at the CCSD(T)/CBS level. Inspection of the $\Delta_t H^{o}_{298}$ values in Table 2 reveals that reaction 7, which breaks P₄S₃ into the bicycle P₂S₂, generates a $\Delta_t H^{o}_{298}$ value which seems to be fairly converged at the W1-F12 level. For example, the difference between the W1-F12 value ($\Delta t H^{\circ}_{298} = -93.8$) and the W3lite-F12 value ($\Delta t H^{\circ}_{298} = -94.5 \text{ kJ mol}^{-1}$) is less than 1 kJ mol⁻¹. Similarly, the difference between W2-F12 and W3lite-F12 is less than 1 kJ mol⁻¹ (Table 2). Equally, reaction 7 emerges as the best option for predicting the enthalpy of formation of the P4S4 isomers with differences between W1-F12 and W3lite-F12 ranging between 3.0–3.7 kJ mol⁻¹ (Table 2). Therefore, hereinafter we will use reaction 7 for predicting the enthalpies of formation of larger phosphorus sulfide cages for which we are only able to calculate the reaction energies using W1-F12 theory.

3.4. CCSD(T)/CBS enthalpies of formation of P₄S₅, P₄S₆, and P₄S₁₀ isomers via thermochemical cycles. The results of Section 3.3 indicate that reaction (7) provides the most reliable enthalpies of formation at the W1-F12 level. Here, we will use this reaction for obtaining the enthalpies of formation of the P₄S_n (n = 5, 6, and 10) isomers for which we were only able to calculate W1-F12 energies. The equivalent of reaction (7) for P₄S₅, P₄S₆, and P₄S₁₀, respectively, are:

0))))
0))

 $P_4S_6 \rightarrow 2 P_2S_2 + S_2 \tag{11}$

 $P_4 S_{10} \to 2 P_2 S_2 + 3 S_2 \tag{12}$

Table 4 gives the W1-F12 enthalpies of formation at 298 K ($\Delta_f H^{\circ}_{298}$) obtained from reactions 10 and 11 for the P4S5 and P4S6 isomers, respectively. The energy differences between the P4S5 isomers are not very large. The α -P4S5 and β -P4S5 isomers are essentially isoenergetic with enthalpies of formation of -126.2 and -126.1 kJ mol⁻¹, respectively. The γ -P₄S₅ isomer is less stable by about 13.4 kJ mol⁻¹. In contrast, the enthalpies of formation of the P₄S₆ isomers are spread over a wider range of 41.2 kJ mol⁻¹, with β -P₄S₆ being the most stable isomer and ϵ -P₄S₆ the least stable isomer.

The Berzelius reagent (P₄S₁₀), the most well-known P₄S_n system, has widespread chemical applications in industry and synthesis as a thionating agent.¹⁹ Nevertheless, its enthalpy of formation is not accurately known. Here, we were able to calculate the energy of P₄S₁₀ at the W1-F12 level. Using an atomization reaction, we obtain an enthalpy of formation of $\Delta_d H^2_{298} = -$ 177.7 kJ mol⁻¹. However, based on the thermochemical insights obtained in sections 3.2 and 3.3 we know that atomization reactions significantly overestimate the enthalpies of formation obtained via reactions that conserve larger chemical environments on the two sides of the reaction. Indeed, using reaction (7) we obtain an enthalpy of formation of -215.4 kJ mol⁻¹ for the Berzelius reagent. The difference of nearly 40 kJ mol⁻¹ between these two values demonstrates the danger of using atomization reactions for calculating enthalpies of formation for large systems containing many second-row atoms. Finally, we note that the available experimental enthalpy of formation for P₄S₁₀ (-228.0 kJ mol⁻¹) is in reasonable agreement with our best theoretical value of -215.4 kJ mol⁻¹.

Compound	Reac.	W1-F12
α -P ₄ S ₅	(10)	-126.2
β-P ₄ S ₅	(10)	-126.1
γ -P4S5	(10)	-112.7
α -P4S6	(11)	-144.7
β -P ₄ S ₆	(11)	-153.9
γ -P4S6	(11)	-134.4
$\delta - P_4 S_6$	(11)	-136.3
ϵ -P ₄ S ₆	(11)	-118.7
$P_{4}S_{10}$	(12)	-215.4

Table 4. W1-F12 enthalpies of formation at 298 K obtained from reactions 10 and 11 for P_4S_5 and P_4S_6 isomers and reaction 12 for P_4S_{10} (kJ mol⁻¹).

3.5. Near-linear correlation between the enthalpies of formation and cage size for the most stable P4S_n isomers. In sections 3.3 and 3.4 we obtained our best enthalpies of formation for the P4S_n isomers via reaction (7). These are summarized in Table 5 for the most stable isomers of each molecular formula. We find that for the most stable isomers there is a near-linear correlation between the enthalpy of formation and the number of atoms in the P4S_n structures, with a squared correlation coefficient of $R^2 = 0.992$ (Figure 3). In particular, we obtain the following linear relationship between $\Delta t H^{0}_{298}$ and the number of S atoms in the P4S_n structure: $\Delta t H^{2}_{298} = -17.616n - 41.022$. This empirical linear relationship can be used for obtaining a ballpark estimate for the most stable P4S_n isomers that are not considered in the present work. For example, using this linear relationship for the P4S_n isomers in Table 5 we obtain $\Delta t H^{2}_{298} = -93.9$ (P4S3), $-111.5 (\alpha - P4S4)$, $-129.1 (\alpha - P4S5)$, $-146.7 (\beta - P4S6)$, and -217.2 (P4S10) kJ mol⁻¹. These approximate values differ from the best estimates in Table 5 by 0.6 (P4S3), $-3.1 (\alpha - P4S4)$, $-2.9 (\alpha - P4S5)$, $7.2 (\beta - P4S6)$, and -1.8 (P4S10) kJ mol⁻¹.

Table 5. Best enthalpies of formation at 298 K ($\Delta_t H^{\circ}_{298}$) obtained from reactions 7, 10, and 11 for the most stable P₄S_n isomers (kJ mol⁻¹).

Compound	Reac.	Wn	$\Delta f H^0$ 298
P_4S_3	(7)	W3lite-F12	-94.5
α -P ₄ S ₄	(7)	W3lite-F12	-108.4
α -P ₄ S ₅	(10)	W1-F12	-126.2
β-P ₄ S ₆	(11)	W1-F12	-153.9
$P_{4}S_{10}$	(12)	W1-F12	-215.4



Figure 3. Near-linear relationship between the enthalpies of formation and cage size for the most stable P_4S_n isomers considered in the present work.

3.6. Evaluation of the performance of lower-level composite ab initio procedures. It is of interest to evaluate the performance of more economical composite ab initio procedures for their ability to accurately calculate the enthalpies of formation of these challenging systems. Here, we

will calculate the enthalpies of formation with the Gn and CBS composite procedures using reactions 7 and 10–12 as recommended in Sections 3.3 and 3.4, rather than via atomization reactions. Table 6 gives an overview of the performance of these procedures.

Table 6. Deviations and overall error statistics from our best enthalpies of formation and isomerization energies by Gn and CBS composite ab initio procedures (kJ mol⁻¹).^{*a,b*}

		G3(MP2)	G3(MP2)B3	G3	G3B3	G4(MP2)	G4(MP2)-6X	G4	CBS-QB3
$\Delta f H^{0}$ 298	RMSD	22.7	12.9	38.8	27.0	10.6	18.2	18.0	27.5
	MAD	20.3	10.8	35.5	24.3	8.3	9.0	16.7	25.2
	MSD	-20.3	-10.8	-35.5	-24.3	-7.5	-8.8	-16.7	-25.2
Isomerization	RMSD	3.7	3.4	4.7	4.3	2.2	2.1	2.5	4.2
	MAD	3.0	2.9	4.3	3.9	1.6	1.8	2.20	3.7
	MSD	-1.6	-1.3	0.2	0.5	-1.5	-0.1	0.11	-0.6

 ${}^{a}\Delta t H^{o}_{298}$ values are calculated using reactions 7 and 10–12 as recommended in Sections 3.3 and 3.4. ${}^{b}RMSD = root-$ mean-square deviation, MAD = mean-absolute deviation, MSD = mean-signed deviation.

We begin by noting that the CBS-QB3 procedure results in poor performance with an overall RMSD of 27.5 kJ mol⁻¹. G3 and G3(MP2), in which the geometries and ZPVEs are obtained at the MP2 and HF levels, respectively, also result in poor performance with RMSDs of 22.7 (G3(MP2)) and 38.8 (G3) kJ mol⁻¹. In contrast, G3B3 and G3(MP2)B3, in which the geometries and ZPVEs are obtained with B3LYP result in improved RMSDs of 12.9 (G3(MP2)B3) and 27.0 (G3B3) kJ mol⁻¹. Interestingly, in both cases the lower-cost Gn(MP2)-type procedure outperforms the more rigorous Gn procedure. The same trend is seen for the G4-type methods for which we obtain RMSDs of 10.6 (G4(MP2)) and 18.0 (G4) kJ mol⁻¹. The G4(MP2)-6X procedure results in similar performance to the G4 procedure. Overall, all the Gn-type and CBS-QB3 methods systematically underestimate our best enthalpies of formation as

indicated by mean-signed deviations in absolute value being equal or close to the mean-absolute deviations.

In contrast to absolute enthalpies of formation, where we obtain RMSDs ranging between 10.6 (G4(MP2)) and 38.8 (G3) kJ mol⁻¹, all of the considered composite procedures give good-to-excellent performance for the isomerization energies with RMSDs below the 5 kJ mol⁻¹ mark. The best performing procedures are G4(MP2) and G4(MP2)-6X with RMSDs of 2.2 and 2.1 kJ mol⁻¹, respectively. In contrast, G3, G3B3, and CBS-QB3 result in RMSDs larger than 4 kJ mol⁻¹.

4. Conclusions

The enthalpies of formation and isomerization energies of P_4S_n molecular cages are not experimentally (or theoretically) well known. Here, we obtain these thermochemical properties for a set of experimentally known P_4S_n cages, where n = 3, 4, 5, 6, and 10, by means of explicitly correlated high-level thermochemical procedures approximating the CCSD(T) and CCSDT(Q) energies at the complete basis set limit. We show that the CCSD and (T) valence correlation components of the atomization reactions converge exceedingly slowly with the size of the oneparticle basis set due to the presence of many second-row atoms in these molecular cages. In addition, the atomization reactions have very significant contributions from post-CCSD(T) correlation effects. Therefore, these cage structures are challenging targets for thermochemical procedures approximating the CCSD(T) energy (e.g., W1-F12, W2-F12, and G4) and it is important to use judiciously selected thermochemical cycles. Based on results obtained at the CCSDT(Q)/CBS level for the smaller cages (P4S₃ and P4S₄) we find that the reaction which decomposes the P4S_n cages to P2S₂ and S₂ is well converged even at the W1-F12 level. We obtain our best enthalpies of formation using this reaction in conjunction with W4 enthalpies of formation for P₂S₂ and S₂ and reaction energies calculated at the CCSDT(Q)/CBS (for P₄S₃ and P₄S₄) or CCSD(T)/CBS (for P₄S₅, P₄S₆, and P₄S₁₀) level of theory. Our best $\Delta t dP^{o}_{298}$ values are – 94.5 (P₄S₃), -108.4 (α -P₄S₄), -98.7 (β -P₄S₄), -126.2 (α -P₄S₅), -126.1 (β -P₄S₅), -112.7 (γ -P₄S₅), -144.7 (α -P₄S₆), -153.9 (β -P₄S₆), -134.4 (γ -P₄S₆), -136.3 (δ -P₄S₆), -118.7 (ϵ -P₄S₆), and -215.4 (P₄S₁₀) kJ mol⁻¹. Interestingly, we find a linear correlation (R² = 0.992) between the enthalpies of formation of the most stable isomers of each molecular formula and the number of atoms in the P₄S_n cages. We use our best $\Delta t dP^{o}_{298}$ values to assess the performance of a number of lower-cost composite ab initio methods. For absolute enthalpies of 10.6 and 12.9 kJ mol⁻¹, respectively. On the other hand, G3, G3B3, and CBS-QB3 give the worst performance, with RMSDs of 27.0–38.8 kJ mol⁻¹. For relative isomerization energies, however, all the considered procedures result in small RMSDs below 5 kJ mol⁻¹. Here, G4(MP2)-6X and G4(MP2) emerge as the best performances with RMSDs of 2.1 and 2.2 kJ mol⁻¹, respectively.

Supplementary data

Diagnostics indicating the importance of post-CCSD(T) correlation effects for the species considered in this work (Table S1); B3LYP-D3/Def2-TZVPP optimized geometries for the species considered in this work (Table S2); a comparison between the CCSD(T)/cc-pV(Q+d)Z and B3LYP-D3/Def2-TZVPP geometries for P4S₃ (Figure S1), and B3LYP-D3/Def2-TZVPP bond distances for the structures in Figure 1 (Figures S2 and S3).

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Conflict of Interest Statement

The authors declare no conflict of interest.

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