The vibronic coupling between the $^3A_2(n\pi^*)$ and the $^3B_2(\pi\pi^*)$ states demonstrates, in contrast, a much larger influence on the out-of-plane susceptibility of the molecule. The energy minimum for the $^3A_2(n\pi^*)$ state corresponds to an out-of-plane conformation which is stabilized with respect to the planar conformation by about 500 cm^{-1} in the CASSCF calculation and by about 1200 cm^{-1} in the UHF calculation.

The $^3A_1(\pi\pi^*)$ state has been shown to be subject to a vibronic coupling which is qualitatively similar to that between the $^3B_{1u}$ and the $^3E_{1u}$ states of benzene. The effect of introducing two nitrogen atoms in the aromatic ring manifests itself most clearly in the stabilization of the quinoidal conformation corresponding to $\varphi = 0°$; the other two quinoidal conformations are 630 cm^{-1} higher in energy, while the antiquinoidal conformations form the saddle points in the trough.

Finally, we have considered the description of the geometry changes in the $n\pi^*$ states in relation to the nature of the π^* orbital to which a lone-pair electron is in first approximation excited. Taking into account as well previous results on the $^3B_1(n\pi^*)$ state of pyridine, it has been shown that the structural response of the molecule to an $n\pi^*$ excitation correlates remarkably well with the nodal-plane structure of the π^* orbital. This structural response shows up partly in the elongation of bonds and partly in out-of-plane distortions. Though an $n\pi^*$ state in azabenzenes by its intrinsic nature seems to be susceptible to out-of-plane deformations, the contribution of such out-of-plane distortions to the total geometry relaxation does not have to dominate the structural response to the excitation.

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Clusters of Phosphorus: A Theoretical Investigation

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Abstract: A variety of phosphorus clusters up to P_{28} has been studied with ab initio SCF and MP2 calculations. Many of the larger clusters are found to be energetically stable with respect to P_4. The more interesting clusters are characterized by their equilibrium structures and NMR chemical shieldings and partially characterized by vibrational spectra to facilitate detection of the molecules. A probable reaction scheme for the formation of red phosphorus from white phosphorus emerges, and possible structural units of red phosphorus are established.

I. Introduction

"Precise molecular structure data for the various forms (of phosphorus) is still limited and although their inter-conversion can, in most cases, be carried out, many of the phenomena involved remain imperfectly understood".[1] Some of these gaps can now be filled with results from large-scale ab initio calculations. Previous attempts were directed toward small clusters up to P_8, which were suspected to be present in the vapor phase along with P_2 and P_4. A notable theoretical contribution came from Jones and Hohl[2] who systematically explored clusters up to P_8 with a simulated annealing technique based on the density functional method. Their most striking results are the prediction of a "cuneane" P_8 molecule as the most stable cluster besides tetrahedral P_4 and the prediction of a moderately stable P_6 cluster with C_{2v} symmetry formed by edge-on addition of P_2 to P_4.

There is no experimental evidence for species other than P_2 and P_4 in the vapor phase obtained from white phosphorus between 300 and 1470 K.[3a] Cationic clusters up to at least P_{24}^+ could be observed by mass spectroscopy in quenched vapor obtained from red phosphorus at 300K.[3b]

In this work we focus attention on even-membered larger phosphorus clusters up to P_{28}. Odd-membered clusters were not investigated, since our aim was to find phosphorus clusters and chain polymers which are energetically more stable than P_4, and radicals are unlikely candidates. Three major types of clusters will be considered: isolated polyhedral clusters, P_4 units linked by single bonds, and polyhedral units linked by two single bonds. From these investigations a consistent scheme of formation and structural features of red phosphorus emerges, which has some bearing on violet (Hittorf) phosphorus.[4] We further obtain hints for the possible existence of P_{12} and P_{16} clusters as new forms of phosphorus.

In our choice of potentially favorable structures we have been guided by chemical intuition and by a wealth of structures of substituted phosphanes[5] and polyphosphides.[6] However, some of those structural units do not lend themselves to medium-sized clusters. This includes the odd-membered subunits P_7 and P_9 which can only occur in larger aggregates unless dangling bonds are saturated.

II. Details of Computation

SCF and MP2 treatments as well as SCF force field calculations to compute vibrational frequencies have been carried out with the program system TURBOMOLE.[7] NMR shielding constants were computed by the SCF/GIAO method[8] with the program SHEILA,[7b] which uses a semidirect algorithm for the solution of coupled-perturbed Hartree–Fock (CPHF) equations for the magnetic field as perturbation.

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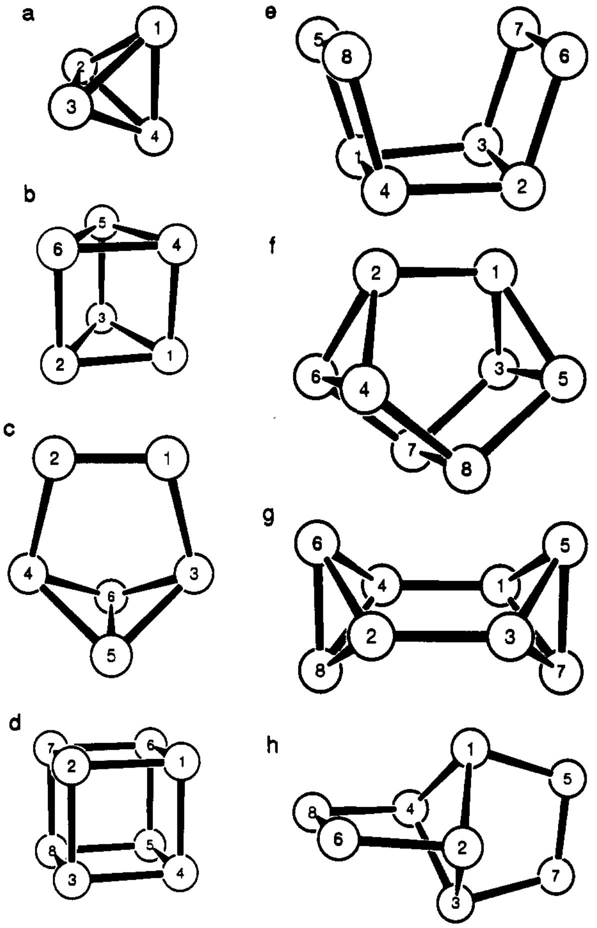

Figure 1. Computed structures of phosphorus clusters P_4 to P_8: (a) P_4 (T_d), (b) P_6 (D_{3h}), (c) P_6 (C_{2v}), (d) P_8 (O_h), (e) P_8 (C_{2v}) ladder-like; (f) P_8 (C_{2v}) cuneane-like, (g) P_8 (D_{2h}), (h) P_8 (D_{2d}).

Basis sets were taken from the new TURBOMOLE basis set library.[9] Three basis sets have been employed for P: split valence plus polarization SVP, {5311/511/1}, $\eta_d = 0.45$; double-ζ plus polarization DZP, {521111/31111/1}, $\eta_d = 0.45$; triple-ζ plus double polarization TZDP, {5121111/51111/11}, $\eta_d = 0.27$ and 0.8. For additional calculations on phosphanes P_4H_2, P_8H_2, and $P_{12}H_2$, a {31} hydrogen basis was used.[10] The SCF structure optimizations, force field calculations, and MP2 treatments were carried out employing the SVP basis throughout. The TZDP basis was mainly used for smaller clusters (P_4 and P_{12}) to check the accuracy of the SVP basis. NMR chemical shifts were treated with DZP and (partly) TZDP basis sets. The calculations were carried out on workstations, IBM Risc 6000, partly with the parallel version[11] of TURBOMOLE using four workstations simultaneously.

III. Energetics of Phosphorus Clusters

The Smaller Clusters P_4 to P_8. Extensive ab initio calculations on tetrahedral P_4, Figure 1a, were aimed at an understanding of its remarkable stability,[2,12] which has few analogues in hydrocarbon chemistry. Today it is well established that inclusion of polarization functions in the basis set is mandatory for a meaningful description of electronic structure and stability of P_4 — and other phosphorus clusters as well. Our calculations on P_4 are only meant as a reference to which other phosphorus clusters will be compared.

The following discussions are based on the SCF/SVP energies collected in Table I; the accuracy of these results will be addressed in a later section.

Table I. Computed SCF/SVP Energies of Phosphorus Clusters P_n

mol	sym	fig	E_{SCF} (au)	ΔE_n[a]	$\Delta E_n/(P_4)$[b]
P_4	T_d	1a	−1362.544 49	0	0
P_6	D_{3h}	1b	−2043.779 39	+98	+65
P_6	C_{2v}	1c	−2043.784 07	+85	+57
P_8	C_{2v}	1e	−2725.016 63	+190	+95
P_8	O_h	1d	−2725.032 13	+149	+75
P_8	D_{2d}	1h	−2725.039 56	+130	+65
P_8	D_{2h}	1g	−2725.041 77	+124	+62
P_8	C_{2v}	1f	−2725.073 18	+42	+21
P_{10}	C_{2v}	4c	−3406.320 99	+106	+42
P_{10}	C_{2h}	7a	−3406.333 21	+74	+29
P_{10}	C_{3v}	3a	−3406.340 79	+54	+22
P_{10}	C_2	3h	−3406.345 98	+37	+15
P_{10}	C_s	4a	−3406.360 05	+3	+1
P_{10}	C_{2v}	6a	−3406.362 19	−3	−1
P_{12}	D_{2d}	5a	−4087.589 30	+116	+39
P_{12}	C_{2v}	4b	−4087.621 35	+32	+11
P_{12}	C_s	5b	−4087.627 71	+15	+5
P_{12}	D_{3d}	3b	−4087.645 51	−32	−11
P_{14}	D_{3h}	3c	−4768.868 47	+98	+28
P_{14}	C_s	6e	−4768.941 66	−94	−27
P_{16}	D_{2h}		−5450.118 28	+157	+39
P_{16}	D_{4d}	3d	−5450.138 68	+103	+26
P_{16}	C_s	7b	−5450.167 46	+28	+7
P_{16}	C_s	5c	−5450.172 49	+14	+4
P_{16}	C_2	6b	−5450.197 42	−51	−13
P_{16}	C_{2h}	5d	−5450.219 43	−109	−27
P_{18}	D_{3h}	3g	−6131.459 48	−24	−5
P_{18}	C_{2v}	6c	−6131.515 88	−172	−38
P_{20}	C_{3v}	3f	−6812.637 20	+224	+45
P_{20}	I_h	3e	−6812.638 92	+219	+44
P_{24}	C_{2v}	5e	−8175.318 78	−136	−23
P_{28}	C_{2v}	6d	−9537.933 14	−319	−46

[a] $\Delta E_n = E_{SCF} - {}^{n}/_{4}E_{SCF}(P_4)$ (kJ/mol). [b] $\Delta E_n/(P_4) = \Delta E_n$ per P_4 unit (kJ/mol).

The most stable six-membered cluster is not the prismane analogue P_6 (D_{3h}), Figure 1b, but the C_{2v} structure, Figure 1c, which can best be described as P_2 added edge-on to P_4 and containing a PP double bond. The present calculations confirm earlier results of Jones and Hohl.[2] Neither of the P_6 clusters is energetically more stable than P_4. A functionalized P_6 molecule, $P_6Cp^*_2$, with two pentamethylcyclopentadienyl rests added to the PP double bond in the P_6 (C_{2v}) structure has been characterized by X-ray structure analysis.[13]

Jones and Hohl[2] describe four structures of P_8 of which the cubane analogue P_8 (O_h), Figure 1d, is among the least stable, Table I. One of the P_8 structures (C_2) found by the density functional method could not be reproduced at the SCF/SVP level: the structure relaxed to one with three fused four-membered rings and two PP double bonds, Figure 1e, which is even less stable than the cubane structure. The most stable P_8 cluster is the cuneane analogue P_8 (C_{2v}), Figure 1f, for the first time identified by Jones and Hohl.[2] They found it to be more stable than $2P_4$ by 46 kJ/mol but were cautious with this conclusion. Our SCF and MP2 calculations confirm this cuneane structure as the most stable P_8 isomer, but we find it energetically less stable than $2P_4$ by 42 kJ/mol. Another interesting geometry[2] is P_8 (D_{2h}), Figure 1g: two P_4 units are added edge to edge. A third isomer of P_8 which is more stable than the O_h structure is P_8 (D_{2d}), Figure 1h. This structure has not been found by simulated annealing based on the density functional method.[2] It shows two PP double bonds and can be obtained from P_6 (C_{2v}) by another edge-on addition of P_2. We conclude the following: no P_8 cluster is stable with respect to $2P_4$; the most stable P_8 clusters are those with symmetries C_{2v} and D_{2h}.

P_4 Units Linked by Single Bonds. In 1952 Pauling and Simonetta[14] suggested that red phosphorus is formed from the white allotrope by breaking only a single bond in the P_4 tetrahedron and then linking P_4 units to an infinite chain. We have studied this possibility by calculations of P_4 oligomers with hydrogen saturating the terminal dangling bonds. The computed energies are given in Table II.

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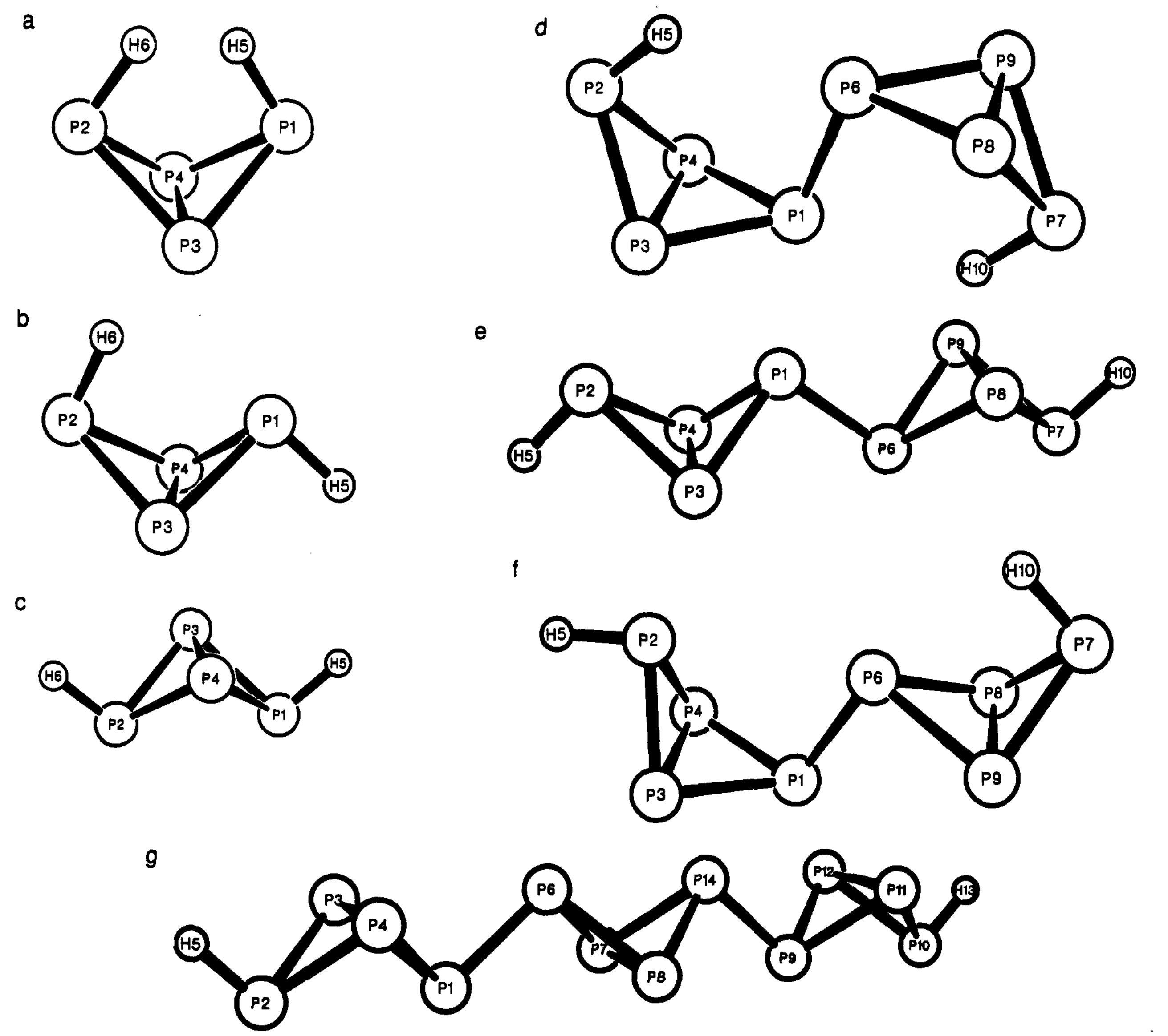

Figure 2. Computed structures of H-(-P_4-)$_k$-H molecules: (a) P_4H_2 (C_{2v}) endo–endo, (b) P_4H_2 (C_s), (c) P_4H_2 (C_{2v}) exo–exo, (d) P_8H_2 (C_{2h}) all-endo, (e) P_8H_2 (C_{2h}) all-exo, (f) P_8H_2 (C_s), (g) $P_{12}H_2$ (C_{2v}).

Table II. Computed SCF/SVP Energies of $P_{4n}H_2$ Compounds

mol	sym	fig	E_{SCF} (au)
P_4H_2	C_{2v}	2a	−1363.67263
P_4H_2	C_{2h}	2b	−1363.67884
P_4H_2	C_{2v}	2c	−1363.67978
P_8H_2	C_{2h}	2d	−2726.19462
P_8H_2	C_{2h}	2e	−2726.22028
P_8H_2	C_s	2f	−2726.21381
$P_{12}H_2$	C_{2h}	2g	−4088.76081

The monomer, P_4H_2,[5,15] comes in three stereoisomers: endo–endo, Figure 2a, endo–exo, Figure 2b, and exo–exo, Figure 2c. The endo–endo isomer is energetically unfavorable due to steric hindrance between the hydrogen atoms: the PPH bond angles are forced to open to 100°. The other two isomers are of comparable stability, with the exo–exo structure more stable at the SCF/SVP level. A previous treatment at the MP2 level using a 6-31G++(d,p) basis[16] has led to the same result. The substituted phosphane P_4R_2 exists in the exo–exo form.[15]

The dimer P_8H_2 resulting from the (unfavorable) endo–endo P_4H_2 forms two (very similar) conformers of which the more symmetric conformer (C_{2h}), Figure 2d, with the lone pairs in anti position is more stable. Only a single structure could be located for the dimer arising from two exo–exo monomers, again in an anti conformation of the lone pairs (C_{2h}), Figure 2e. This molecule is energetically favored over the dimer built from the endo–endo monomers by 67 kJ/mol. It can thus be concluded that an exo–exo linkage is preferred compared to an endo–endo linkage. We further studied the linkage of two endo–exo forms head to tail. The only stable geometry found is shown in Figure 2f (with C_s symmetry). This alternative is less stable than the exo–exo dimer and confirms that the exo–exo linkage of two P_4 units with lone pairs in the anti position is most stable.

With these results for the energetics of isomers and conformers of P_4H_2 and P_8H_2 we restricted our study of $P_{12}H_2$ to the isomer shown in Figure 2g, which has exo–exo linkages only and exhibits two trans conformations. The structural parameters of the central P_4 unit vary very little from those in the terminal units, or from those in P_8H_2. We thus conclude that

$$E(-P_4-) - E(P_4) \approx E(P_{12}H_2) - E(P_8H_2) - E(P_4) = 10\ \text{kJ/mol} \quad (1)$$

is a good approximation of the energy per P_4 unit in the polymer suggested by Pauling and Simonetta, which implies that $(-P_4-)_\infty$ is less stable than white phosphorus by about 10 kJ/mol (P_4). Infinite chains of P_4 (of this kind) are not a likely intermediate in the formation of red phosphorus and are probably not formed at all.

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Table III. Computed SCF (Harmonic Approximation) Zero Point Vibrational Energies (ZPVE) and MP2 Energy Contributions E_{corr} (All Core Electrons Frozen) Obtained with the SVP Basis

mol	sym	fig	E_{corr} (au)	ΔE_n (kJ/mol)[a]	ZPVE (kJ/mol)
P_4	T_d	1a	−0.451 55	0	18
P_6	D_{3h}	1b	−0.661 73	+139	30
P_6	C_{2v}	1c	−0.680 66	+77	29
P_8	O_h	1d	−0.869 60	+237	42
P_8	D_{2h}	1g	−0.911 61	+101	
P_8	C_{2v}	1f	−0.904 48	+38	42
P_8	D_{2d}	1h	−0.903 66	+128	41
P_{10}	C_{3v}	3a	−1.127 81	+56	54
P_{10}	C_2	3h	−1.140 48	+10	54
P_{10}	C_{2v}	6a	−1.145 16	−45	53
P_{10}	C_s	4a	−1.143 56	−35	54
P_{12}	C_s	5b	−1.377 28	−44	
P_{12}	D_{3d}	3b	−1.375 26	−86	67
P_{14}	C_s	6e	−1.609 37	−170	
P_{16}	C_{2h}	5d	−1.845 38	−212	
P_{16}	C_2	6b	−1.840 02	−140	
P_{18}	C_{2v}	6c	−2.071 50	−276	
P_{20}	I_h	3e	−2.310 47	+81	110

[a] $\Delta E_n = E - {}^n/_4E(P_4)$ (kJ/mol), computed reaction energies at the MP2 level.

Table IV. SCF and MP2 (All Core Electrons Frozen) Energies Computed with the Extended TZDP Basis at SCF/SVP Geometries

mol	sym	fig	E_{SCF} (au)	E_{corr} (au)	ΔE_{SCF}[a]	ΔE_{MP2}[a]
P_4	T_d	1a	−1363.020 65	−0.50227	0	0
P_8	C_{2v}	1f	−2726.020 01	−1.01185	+56	+36
P_{12}	D_{3d}	3b	−4089.061 11	−1.53250	+2	−66
P_{16}	C_{2h}	5d	−5452.105 70		−61	
P_{20}	I_h	3e	−6815.001 15		+268	

[a] $\Delta E = E(P_n) - {}^n/_4E(P_4)$ (kJ/mol).

Polyhedral Clusters P_{10} to P_{20}. The energies of the clusters to be discussed now are collected in Table I. P_{10} (C_2), Figure 3h, is found to be comparable in stability to P_8 (C_{2v}) and is unstable with respect to ${}^5/_2P_4$. Slightly higher in energy is P_{10} (C_{3v}), Figure 3a. P_{12} (D_{3d}), Figure 3b, seems to be the most stable polyhedral phosphorus cluster. In particular it is more stable than $3P_4$ within the SCF/SVP and MP2/SVP approximations. Six puckered five-membered rings with bond angles close to the preferred values between 95° and 100°, Table VI, provide an intuitive rationalization of this finding. To confirm our result we also performed single point SCF and MP2 calculations with the extended TZDP basis at the SCF/SVP geometry and included SCF/SVP zero point vibration effects (harmonic approximation). P_{12} (D_{3d}) is stable against dissociation in to $3P_4$ by 53 kJ/mol on this level, as shown in Table V. Computed properties of P_{12} are documented in Table VI and are available as supplementary material.

The higher polyhedral clusters P_{14} (D_{3h}), Figure 3c, P_{16} (D_{4d}), Figure 3d, and the dodecahedral P_{20} (I_h), Figure 3e, were found to be unstable with respect to decomposition into P_4. Reasons for this behavior may be the presence of four-membered rings, an increasingly planar coordination of phosphorus, and/or the increase in bond angles to 108° in P_{20} (I_h), which is unstable despite an all five-membered ring structure. Large bond angles are partly avoided in the C_{3v} structure of P_{20}, Figure 3f, where one phosphorus lone pair points into the polyhedron. This structure was found to be even less stable than the I_h structure, Table I.

One higher polyhedral cluster, P_{18} (D_{3h}), Figure 3g, was found to be energetically more stable than P_4 at the SCF/SVP level but less stable than P_{12} (D_{3d}). The structure of P_{18} may be related to that of P_{12} (D_{3d}): if one of the three-membered rings in P_{12} is removed, and the resulting open P_9 cage is fused with another P_9 cage, one obtains P_{18}. In comparison to P_{12} it suffers again from too large bond angles.

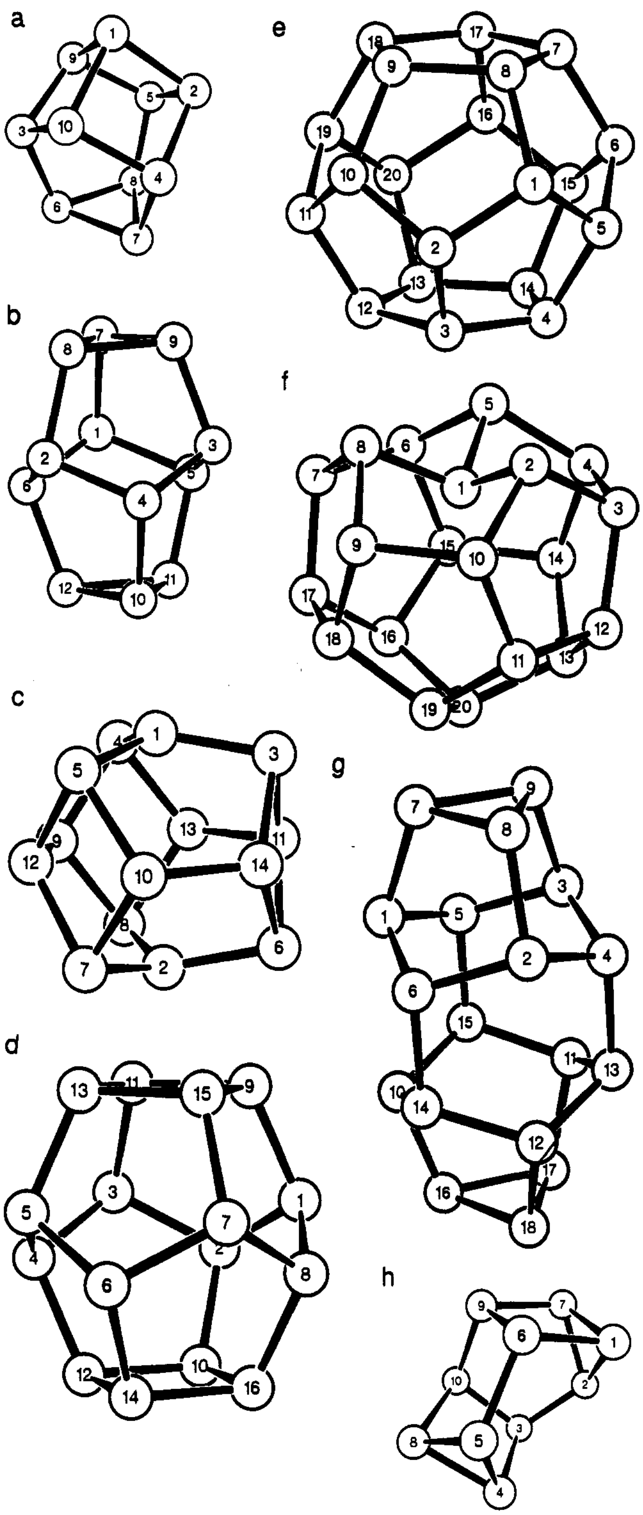


Figure 3. Computed structures of polyhedral phosphorus clusters P_{10} to P_{20}: (a) P_{10} (C_{3v}), (b) P_{12} (D_{3d}), (c) P_{14} (D_{3h}), (d) P_{16} (D_{4d}), (e) P_{20} (I_h), (f) P_{20} (C_{3v}), (g) P_{18} (D_{3h}), (h) P_{10} (C_2).

Phosphorus Clusters Containing PP Double Bonds. Besides the smaller clusters P_6 (C_{2v}), Figure 1c, and P_8 (D_{2d}), Figure 1h (which originate from P_4 by adding one or two P_2 molecules, respectively), we also investigated three medium-sized clusters with PP double bonds: P_{10} (C_s), Figure 4a, P_{12} (C_{2v}), Figure 4b, and P_{10} (C_{2v}), Figure 4c. These are obtained from the cuneane analogue P_8 (C_{2v}) by adding P_2.

P_{10} (C_s) is of comparable stability as P_4, Table I. This surprise (in view of the PP double bond) can be rationalized as the release of ring strain from the two adjacent four-membered rings present in P_8 (C_{2v}), a constellation which proved especially unfavorable in P_8 (O_h). This interpretation is supported by the notion that a second P_2 molecule added to yield P_{12} (C_{2v}) leads to destabilization, Table I. The calculated properties of P_{10} (C_s) are given in Table VI and are available as supplementary material. We

Table V. Comparison of Reaction Energies Obtained at Various Levels of Approximation (in Parentheses: MP2 Contributions Only)

		SVP		TZDP		
reaction[a]	fig	SCF	MP2	SCF	MP2	TZDP MP2 + ZPVE[b]
$1.5P_4 \rightarrow P_6$ (C_{2v})	1b	86	77 (−9)	96	88 (−9)	90
$2P_4 \rightarrow P_8$ (C_{2v})	1f	42	38 (−4)	56	36 (−10)	42
$3P_4 \rightarrow P_{12}$ (D_{3d})	3b	−32	−86 (−54)	2	−66 (−68)	−53
$4P_4 \rightarrow P_{16}$ (C_{2h})	5d	−109	12 (−103)	−61		
$5P_4 \rightarrow P_{20}$ (I_h)	3e	219	−81 (−138)	268		

[a] Molecules are designated as shown in the corresponding figures. [b] ZPVE: zero point vibrational energies, taken from Table III.

Table VI. Computed SCF/SVP Bond Distances and Angles of the Most Stable Phosphorus Clusters[a]

mol	sym	fig	structural parameters
P_4	T_d	1a	1–2 218.9 (220.8)
P_8	C_{2v}	1f	1–2 222.5, 1–3 220.6, 3–5 229.2, 3–7 225.8, 7–8 222.8 4–8–5 105.9
P_{10}	C_{2v}	6a	1–2 221.5, 1–3 222.5, 3–5 221.5, 3–6 221.8, 5–6 222.4 3–1–8 100.3, 1–3–6 105.2, 3–5–4 92.9, 3–6–4 92.8
P_{10}	C_s	4a	1–2 224.5, 1–3 221.5, 2–4 223.6, 3–7 222.1, 3–10 224.9, 4–6 226.0, 4–8 225.2, 7–8 225.8, 9–10 201.4 1–2–4 106.7, 3–1–5 99.4, 1–3–10 99.7, 3–7–6 96.2
P_{12}	D_{3d}	3b	1–5 222.2 (221.1), 1–7 223.8 (221.6), 7–8 225.2 (228.0), 5–1–6 106.3 (106.9), 5–1–7 101.8 (101.5)
P_{14}	C_s	6e	1–2 224.1, 1–3 223.6, 2–4 222.1, 3–5 226.1, 3–7 225.0, 4–8 221.3, 4–10 222.6, 7–8 226.5, 9–10 225.1, 9–11 222.0, 11–13 221.4, 11–14 221.8, 13–14 222.8 2–1–3 106.6, 2–4–8 100.1, 4–2–6 99.6, 2–6–9 101.8, 6–9–11 100.2, 9–11–13 110.0, 11–13–12 93.2
P_{16}	C_{2h}	5d	1–2 225.0, 1–3 224.3, 2–4 221.5, 3–5 225.7, 3–7 225.1, 4–8 220.3, 4–13 224.0, 7–8 227.2 2–1–3 106.6, 4–2–6 105.6, 2–4–13 107.9, 7–6–14 104.4
P_{16}	C_2	6b	1–2 224.9, 1–3 226.6, 1–5 223.7, 4–6 223.3, 5–6 224.6, 5–7 222.1, 6–8 222.0, 8–9 222.5, 9–7 222.4, 7–10 221.2, 8–10 221.3, 9–10 222.4 1–2–4 86.7, 1–3–4 85.9, 2–1–5 100.6, 3–1–5 92.9, 2–4–6 100.8, 1–5–7 103.5, 4–6–8 103.6, 6–8–10 110.4, 7–10–8 93.5, 6–8–9 104.1
P_{18}	C_{2v}	6c	1–2 224.1, 1–3 223.7, 2–4 222.3, 3–5 226.2, 3–7 224.9, 4–8 221.6, 4–18 222.2, 7–8 226.5, 17–18 228.7 1–2–4 99.2, 2–4–8 100.0, 2–4–18 98.0, 8–4–18 98.0, 4–18–14 102.2
P_{28}	C_{2v}	6d	1–2 224.1, 1–3 223.7, 2–4 222.3, 3–5 226.3, 3–7 224.9, 4–8 221.6, 4–15 222.3, 7–8 226.6, 9–10 224.5, 9–24 229.9, 10–13 222.7, 10–14 220.9, 12–13 231.1, 14–15 227.4 1–2–4 99.2, 2–1–5 106.7, 2–4–15 102.4, 8–4–15 98.1, 11–9–24 99.4, 9–11–12 98.8, 4–15–11 101.6, 15–11–9 104.8

[a] Atoms are labeled as in corresponding figures. Bond distances are in pm and angles in deg. MP2/SVP results are given in parentheses as far as available.

note that $P_{14}R_4$, where organic rests R have been added to the double bonds, has been described in ref 5 (structure 67).

An isomeric form of P_{10}, Figure 4c, where P_2 has been added to the bond fusing the two four-membered rings in P_8 (C_{2v}), is found to be energetically much less favorable due to the five-membered rings now being forced into a near-planar conformation. Analogous structures will therefore not be considered further in this work.

P_4 Units Linked by Two Single Bonds. The smallest cluster of this type has already been mentioned: it is P_8 (D_{2h}), Figure 1g, the dimer of tetrahedral P_4. Having this structure in mind we introduce the mnemotechnic notation $P_4{=}P_4$ for this molecule. The equal sign "=" indicates two single bonds which connect the two (distorted) tetrahedrons. Note that two bonds have to be broken and two bonds have to be formed to obtain $P_4{=}P_4$ from $2P_4$ while the nuclear rearrangement involved is small. For the energetics of the (endothermic) reaction consult Table I.

It is now possible to form oligomeric clusters of P_4 in the same way to obtain the trimer $P_4{=}P_4{=}P_4$, P_{12} (D_{2d}), Figure 5a, in an exothermic reaction, and $P_4{=}P_4{=}P_4{=}P_4$, P_{16} (D_{2h}), not shown, in an endothermic reaction, Table I. The probable reason for the destabilization of this tetramer, P_{16}, is the occurrence of boat-shaped six-membered rings with some phosphorus lone pairs pointing at each other more than, e.g., in the dimer where bond angles allow the lone pairs to point into less crowded space.

Thus there is probably no stable polymeric form $({=}P_4{=})_\infty$ as there is probably no $(-P_4-)_\infty$ with P_4 units linked by single bonds as discussed earlier.

P_8 Units Linked by Two Single Bonds. The hypothetic dimer of P_4, $P_4{=}P_4$ or P_8 (D_{2h}), Figure 1g, may be stabilized by addition of another P_4 tetrahedron as discussed before or by isomerization to P_8 (C_{2v}), Figure 1f, the most stable P_8 cluster. Again two bonds

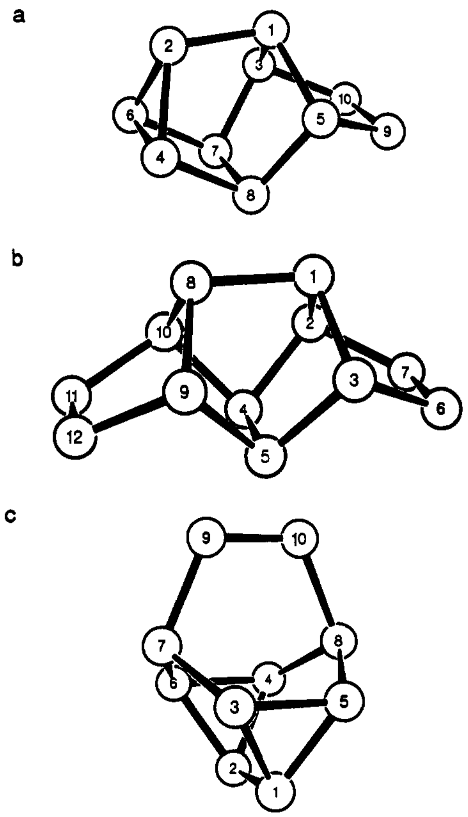


Figure 4. Computed structures of phosphorus clusters containing PP double bonds: (a) P_{10} (C_s), (b) P_{12} (C_{2v}) $P_2{=}P_8{=}P_2$, (c) P_{10} (C_{2v}).

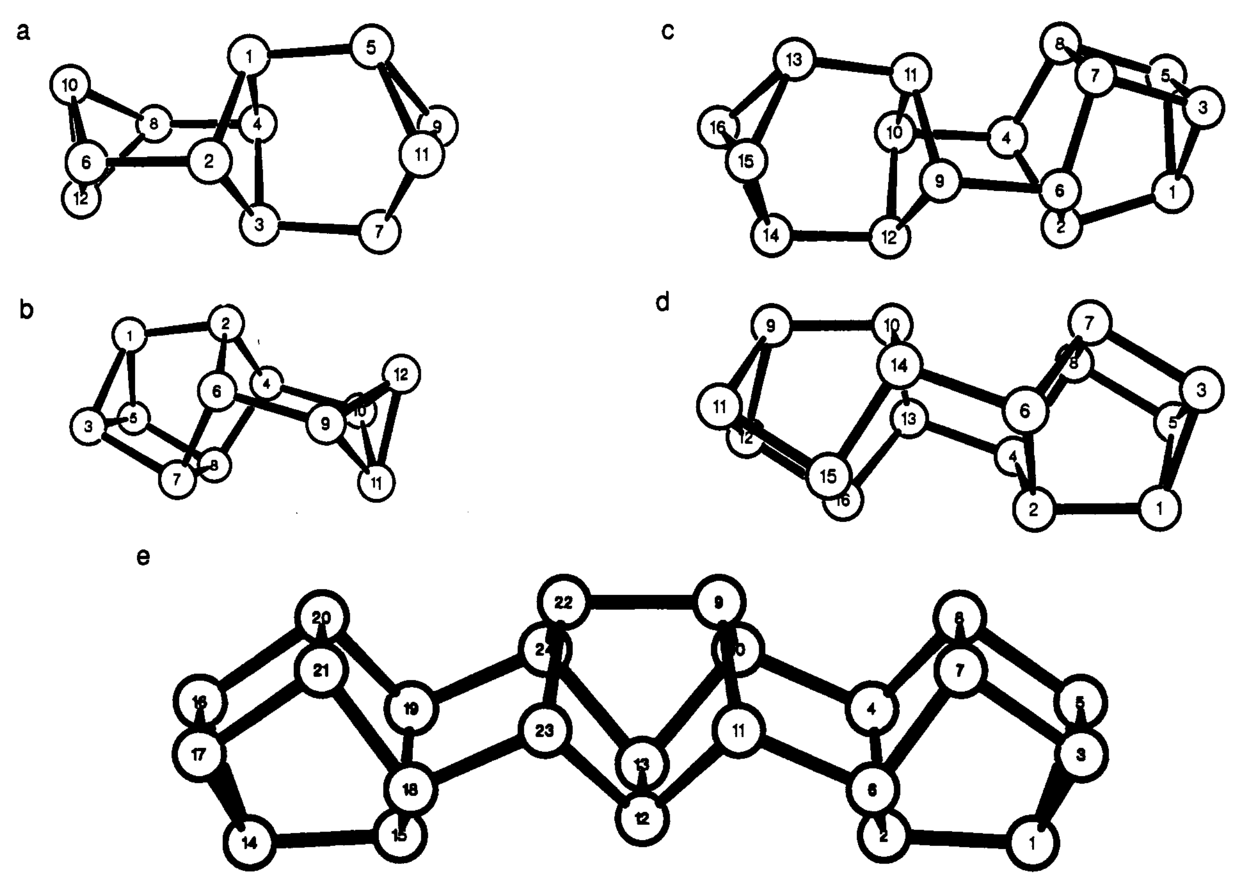


Figure 5. Computed structures of phosphorus clusters built from P_4 and P_8 units linked by two single bonds: (a) P_{12} (D_{2d}), (b) P_{12} (C_s), (c) P_{16} (C_s), (d) P_{16} (C_{2h}), (e) P_{24} (C_{2v}).

have to be broken and two new bonds have to be formed.

As for $P_4{=}P_4$, one can stabilize P_8 (C_{2v}) by adding another P_4 tetrahedron. The resulting molecule, P_{12} (C_s), i.e., $P_8{=}P_4$, Figure 5b, comes close to $3P_4$ in stability at the SCF/SVP level, Table I, and is found to be more stable than $3P_4$ at the MP2 level, Table III. The source of stabilization is the same as that in the formation of P_{10} (C_s) (which we may also term $P_8{=}P_2$) discussed earlier. Further addition of another P_4 molecule to yield $P_8{=}P_4{=}P_4$ (or P_{16} (C_s)), Figure 5c, proceeds almost isoenergetically; the corresponding molecules are 15 and 14 kJ/mol higher than nP_4, respectively, Table I.

$P_8{=}P_4{=}P_4$ can be greatly stabilized by the isomerization to $P_8{=}P_8$ (P_{16} (C_{2h})), Figure 5d, similar to the formation of P_8 (C_{2v}) from $P_4{=}P_4$. $P_8{=}P_8$ is the most stable phosphorus cluster considered so far (in this work) and is considerably more stable than $4P_4$ (by 109 kJ/mol at the SCF/SVP level), Table I. Properties of $P_8{=}P_8$ are listed in Table VI and are available as supplementary material (NMR shifts).

To address the question if $P_8{=}P_8$ continues to polymerize to form $({=}P_8{=})_\infty$, we also calculated the trimer $P_8{=}P_8{=}P_8$ or P_{24} (C_{2v}), Figure 5e, Table I. Surprisingly we found $P_8{=}P_8{=}P_8$ to be slightly less stable than $P_8{=}P_8$, with energies (relative to P_4) of −23 kJ and −27 kJ per mole of P_4, respectively, Table I. This is again similar to the situation with the clusters $P_8{=}P_2$ (or P_{10} (C_s), Figure 4a) and $P_2{=}P_8{=}P_2$ (or P_{12} (C_{2v}), Figure 4b) where addition of a second P_2 molecule to $P_8{=}P_2$ does not lead to further gain in energy.

The energy of $({=}P_8{=})_\infty$ as calculated from $P_8{=}P_8{=}P_8$ and $P_8{=}P_8$

$$E({=}P_8{=}) - 2E(P_4) \approx E(P_8{=}P_8{=}P_8) - E(P_8{=}P_8) - 2E(P_4) = -27\ \text{kJ/mol} \quad (2)$$

is nevertheless below the energy of P_4, but it is above the energy of $P_8{=}P_8$.

Alternating P_4 and P_2 Units Linked by Two Single Bonds. $P_4{=}P_2$ or P_6 (C_{2v}), Figure 1c, may be viewed as the monomeric building block of a polymeric form of phosphorus. The first oligomers (without P=P double bonds) are $P_4{=}P_2{=}P_4$ (P_{10} (C_{2v})), Figure 6a, which is of comparable stability as P_4, Table I, and $P_4{=}P_2{=}P_4{=}P_2{=}P_4$ (P_{16} (C_2)), Figure 6b. The latter is more stable than $4P_4$ by 51 kJ/mol at the SCF/SVP level, Table I. Some calculated properties of these molecules are given in Table VI and as supplementary material.

A crude estimate for the stability of an infinite chain $({=}P_4{=}P_2{=})_\infty$ is obtained from the energy difference between $P_4{=}P_2{=}P_4{=}P_2{=}P_4$ and $P_4{=}P_2{=}P_4$:

$$E({=}P_4{=}P_2) - 1.5E(P_4) \approx E(P_4{=}P_2{=}P_4{=}P_2{=}P_4) - E(P_4{=}P_2{=}P_4) - 1.5E(P_4) = -49\ \text{kJ/mol} \quad (3)$$

which corresponds to −32 kJ/mol per P_4 unit. This hypothetic polymer is the energetically most stable form of phosphorus discussed up to this point.

Alternating P_8 and P_2 Units Linked by Two Single Bonds and Related Clusters. The stability of $P_8{=}P_2$ (P_{10} (C_s)), Figure 4a, has been discussed before. It, too, may be viewed as a unit of a polymeric form of phosphorus, $({=}P_8{=}P_2{=})_\infty$, of which the first oligomers (without PP double bonds) are $P_8{=}P_2{=}P_8$ (P_{18} (C_{2v})), Figure 6c, and $P_8{=}P_2{=}P_8{=}P_2{=}P_8$ (P_{28} (C_{2v})), Figure 6d. These are the most stable phosphorus clusters we found, Table I. Their properties, as far as we could calculate them, are given in Table VI and as supplementary material. From the energies of P_{28} and P_{18} we estimate the energy of the polymer:

$$E({=}P_8{=}P_2{=}) - 2.5E(P_4) \approx E(P_8{=}P_2{=}P_8{=}P_2{=}P_8) - E(P_8{=}P_2{=}P_8) - 2.5E(P_4) = -147\ \text{kJ/mol} \quad (4)$$

The clusters P_{18} (C_{2v}) and P_{28} (C_{2v}) are probably difficult to obtain (despite their stability relative to P_4) because the hypothetic polymer $({=}P_8{=}P_2{=})_\infty$ has an even lower energy per phosphorus atom (eq 4). Any conditions under which P_{18} (C_{2v}) and P_{28} (C_{2v}) are formed would thus probably also promote the growth of longer chains. We note, however, that $P_8{=}P_2{=}P_8$ and $P_8{=}P_2{=}P_8{=}P_2{=}P_8$ are bent (and not linear structures in their equilibrium geometries),

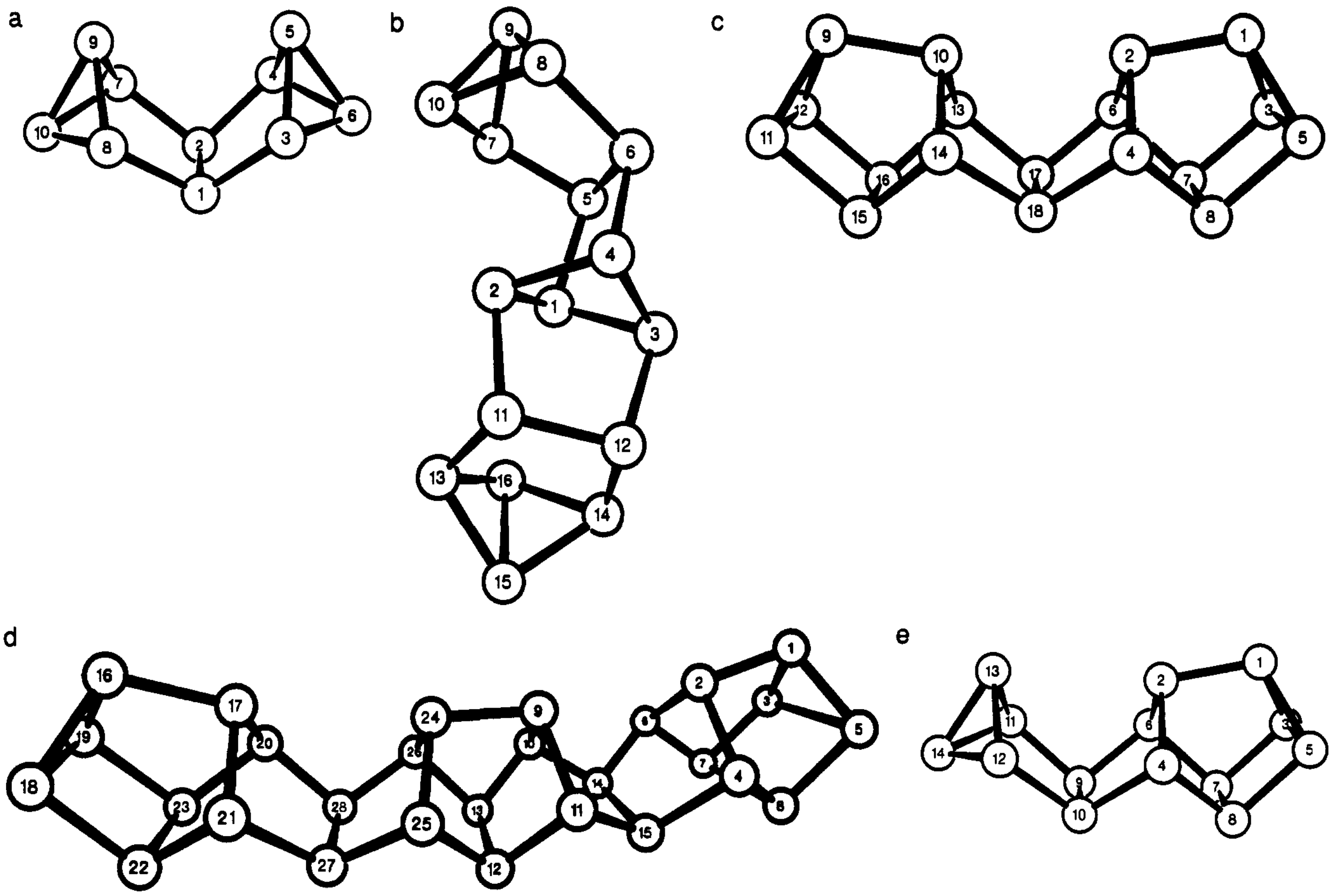


Figure 6. Computed structures of phosphorus clusters built from P_4 or P_8 units linked by P_2 units: (a) P_{10} (C_{2v}), (b) P_{16} (C_2), (c) P_{18} (C_{2v}), (d) P_{28} (C_{2v}), (e) P_{14} (C_s).

and regular chain growth would probably not lead to a simple lattice structure.

We also note the similarity between $(P_8{=}P_2)_n{=}P_8$ and the building blocks of Hittorf's violet phosphorus[4] which contains $({=}P_8{=}P_2{=}P_9{=}P_2{=})_n$ chains, with the P_9 units interconnecting with other chains, building a complicated three-dimensional network. The P_9 units probably straighten the otherwise bent ${=}P_8{=}P_2{=}$ structures and thus allow linear chains with minimum strain. This has first been suggested in ref 4.

Other than with $({=}P_4{=}P_2{=})_\infty$ the growth of $({=}P_8{=}P_2{=})_\infty$ polymers cannot be nourished by a supply of P_8 (C_{2v}) molecules since they are significantly less stable than P_4. Fortunately, however, intermediate clusters like $P_8{=}P_2{=}P_4$ (or P_{14} (C_s)), Figure 6e, can be expected to be very stable (with respect to P_4), Table I.

Other Clusters. We studied two clusters which do not fit into any of the categories mentioned so far. The first of them is P_{10} (C_{2h}), Figure 7a. Its energy is unfavorable, Table I. The other cluster is $P_{12}{=}P_4$ (P_{16} (C_s)), Figure 7b, that is, a P_4 tetrahedron added to the stable P_{12} (D_{3d}) cluster, Figure 3c. There are, of course, three different kinds of bonds in P_{12} to add on, but we studied only the approach considered most likely which opens one of the three-membered rings in P_{12}. The addition reaction proves to be endothermic by 59 kJ/mol (P_{16}). P_{12} (D_{3d}) thus is probably kinetically stable against attack by P_4.

IV. Computed Properties and Accuracies

So far we have mainly discussed SCF energies obtained with an SVP basis set (for SCF/SVP optimized structures, of course). SVP is the smallest type of basis set for which reasonable results can be expected. We have performed additional SCF/TZDP calculations of equilibrium geometries for P_4 and P_{12} (D_{3h}) which result in only minor changes in structure constants, e.g., bond shortenings change by ≤ 1 pm.

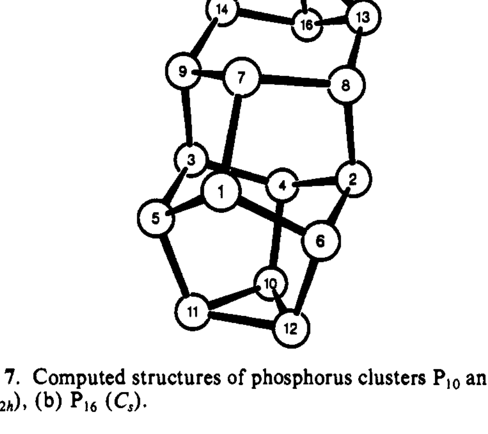
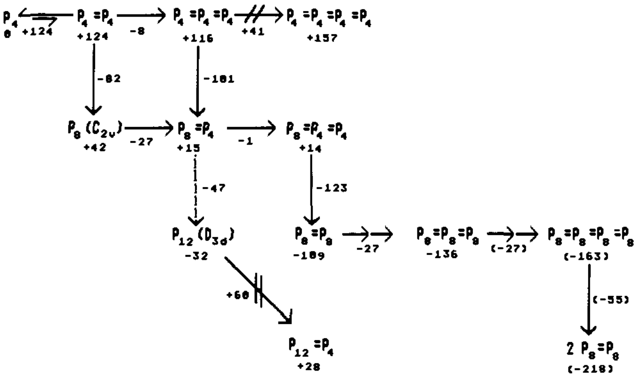


Figure 7. Computed structures of phosphorus clusters P_{10} and P_{16}: (a) P_{10} (C_{2h}), (b) P_{16} (C_s).

The main source of error in computed structure constants thus arises from effects of electron correlation. The deviation between the experimental bond distance of P_4, 221 ± 2 pm[1] (incidentally virtually identical to the MP2/SVP value of 220.8 pm), and the SCF/SVP value, 218.9 pm, amounts to 2 pm. This indicates a typical error of 3 pm in computed bond distances, at least for the reasonably stable isomers with "normal" bonding situations. We likewise expect bond angles on the SCF/SVP level to be in error by typically up to 3°. This conclusion has been checked by an MP2/SVP treatment for P_{12} (D_{3d}) documented in Table VI. The

Scheme I[a]



Reaction Scheme A

[a] A possible reaction scheme for the polymerization of phosphorus involving P_4 only. Energies have been calculated at the SCF/SVP level of theory and are given in kJ/mol relative to the energy of n P_4; energies in brackets are authors estimates.

deviations between SCF and MP2 structure constants are smaller than 3 pm and 1°, and it appears that electron correlation tends to shorten the shorter and to lengthen the longer bonds.

In Table III we have collected MP2/SVP energies and SCF/SVP zero point vibrational energies. In all cases listed only real frequencies were found and therefore the corresponding structures are local minima on the SCF/SVP surface. In Table IV we report for a few selected cases SCF and MP2 energies obtained with the extended TZDP basis, at the SCF/SVP geometries, as a further check. The following trends can be extracted from these results, Tables III and IV:

(i) With the SVP basis one overestimates the stability of the larger clusters relative to the extended TZDP basis by about 10 ± 3 kJ per mole of P_4 on the SCF level. This trend could be attributed to basis set superposition effects present with the smaller SVP basis or the fact that the SVP basis underestimates the stability of P_4.

(ii) MP2/SVP contributions always stabilize the more stable of the larger clusters by roughly 21 ± 5 kJ per mole of P_4. As far as can be seen from the few results — for P_8 (C_{2v}) and P_{12} (D_{3d}) — the MP2 stabilization of the more stable larger clusters is underestimated by the SVP basis (not unexpectedly) as compared to the TZDP basis.

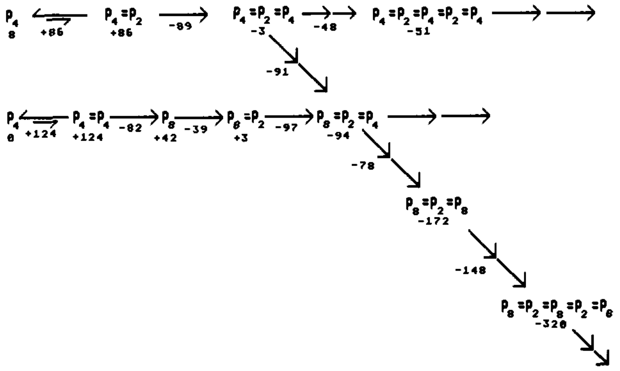
(iii) The two above comments suggest that the MP2/SVP results, Table III, may slightly overestimate the stability of the (more stable) larger clusters.

The computed SCF/SVP vibrational wavenumbers of P_4 (in comparison to experiment[17]) are, in cm^{-1}, e 403 (360), t_2 511 (450), and a_1 672 (600). SCF/SVP overestimates the frequencies by 12–14%, and this may be expected to hold also for the stiffer modes of the other clusters, available as supplementary material.

It is hard to estimate errors of computed NMR chemical shifts[18] (available as supplementary material). We can only offer our personal judgement that deviations from experiment should typically be less than 30 ppm for the TZDP basis (mainly effects of electron correlation), provided solvent effects are negligible. NMR shieldings, σ, obtained with the smaller DZP basis are systematically larger than for the TZDP basis. The deviation appears to increase if σ decreases. Computed shielding constants show an obvious correlation with the sum of bond angles of corresponding phosphorus atoms: the smaller the sum of bond angles the larger the shielding and the smaller the chemical shift.

The above comments in mind we report the most important structure constants in Table VI. SCF/SVP vibrational frequencies and IR intensities are available as supplementary material (or on request from the authors) for all cases for which the ZPVE has been given in Table III.

Scheme II[a]



Reaction Scheme B

[a] A possible reaction scheme for the polymerization of phosphorus involving P_2 and P_4. Energies have been calculated at the SCF/SVP level of theory and are given in kJ/mol relative to the energy of n P_4; energies in brackets are authors estimates.

V. Discussion

From the data gathered, a coherent picture emerges as to how white phosphorus could react to form larger clusters and finally polymeric forms of phosphorus (red phosphorus). Two hypothetical reaction pathways are presented in Schemes I and II. They represent possible cascades of increasingly stable intermediate aggregates. The formation of the first intermediate (start up reaction), however, is always endothermic, well in accord with the kinetic stability of white phosphorus.

Scheme I involves only reactions where two bonds are broken and two bonds are formed in each step. This pathway would possibly yield two stable clusters $P_8{=}P_8$, Figure 5d, and P_{12} (D_{3d}), Figure 3b. The latter cluster, however, can be derived from $P_8{=}P_4$, Figure 5b, only by breaking three bonds.

Scheme II suggests P_2 as an intermediate, at least in a start up reaction. No islands of particularly stable oligomers exist. Instead there is always an energy gain by further cluster growth, yielding a variety of inhomogeneous polymeric phosphorus chains of which $({=}P_4{=}P_2{=})_\infty$ and $({=}P_8{=}P_2{=})_\infty$ are two well-defined limiting cases. Other possible repeating units comprise ${=}P_8{=}P_8{=}P_2{=}$ and ${=}P_{10}{=}P_2{=}$ where the P_{10} subunit is derived from $P_{14}R_4$.[19] In the chains there may be further interspersed structural subunits like P_7, as in $(Ph_4P)_2P_{16}$,[6,20] or P_9, as in Hittorf's violet phosphorus,[4] or various (substituted) phosphanes[5,21] thus allowing for cross-links between chains.

VI. Conclusions

The application of ab initio methods presented in this work has for the first time shed some light on phosphorus chemistry between P_8 and P_∞, which has been a terra incognita so far. This effort involved extensive calculations on 39 species (32 phosphorus clusters and 7 phosphanes) ranging in size up to P_{28} (the largest cluster previously tackled by ab initio methods was P_8[2]). In the choice and design of clusters and their structural features we have been led by chemical intuition and cannot claim completeless. Although further treatments will certainly extend our knowledge, these will hardly affect the basic result of the present study: the first characterization of phosphorus clusters which are energetically stable with respect to decomposition into P_4, which in turn allow one to estimate the stability of possible polymers, eqs 1–4.

A wealth of data has been obtained from which a consistent picture of phosphorus emerges: an old hypothesis on structure and formation of red phosphorus has been refuted,[14] and new hypotheses have been suggested which have passed the tests ab

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initio quantum chemistry can provide by itself at present (a detailed investigation of reactions would require considerably larger efforts). Two medium-size phosphorus clusters, P_{12} (D_{3d}) and the $P_8{=}P_8$ structure of P_{16} (C_{2h}), have been established as particularly stable under appropriate conditions.

The calculated properties (equilibrium structures, IR and Raman spectra, and NMR shieldings) should allow experimentalists to positively identify some of the clusters or the structural units in red phosphorus. The expected range of error for calculated bond lengths is 3 pm, for bond angles 3°, for (stiff) vibrational frequencies 10–15% (systematically too high), and around 30 ppm for relative chemical shieldings. These estimates arise from comparison with experiment for P_4 and from the fact that SCF/TZDP geometries vary by only 1 pm from SCF/SVP for P_4 and P_{12}. Since the stable clusters form a relatively uniform class of compounds (PP single bond distances are between 220 and 231 pm throughout), it may be safely expected that trends in computed properties are reliably described.

After submission of this manuscript, a density functional study on phosphorus clusters P_9 to P_{11} was published.[22] The cluster P_{10} (C_{2v}), Figure 6a, which according to our study is the most stable P_{10} isomer, has not been found in ref 22.

Acknowledgment. We are indebted to Dr. F. Haase for performing the MP2 geometry optimization on P_{12} and to Professor M. Baudler for making unpublished material available to us. This work has been supported by the Fonds der Chemischen Industrie.

Supplementary Material Available: SCF/SVP vibrational frequencies for all molecules listed in Table III, if zero point vibrational energies are given, and NMR shielding constants σ and chemical shifts δ (in ppm) calculated with TZDP or DZP basis sets at the SCF/SVP geometries for the clusters depicted in Figures 1a, 1f, 1h, 3b, 3e, 4a, 5d, and 6a–6e (5 pages). Ordering information is given on any current masthead page.

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π-Bond Strengths of $H_2X{=}YH_2$: X = Ge or Sn, and Y = C, Si, Ge, or Sn

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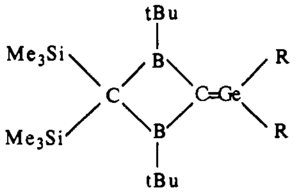
Abstract: The molecular structures and π-bond strengths are determined using both MP2 and MCSCF + CI energies for a series of $H_2X{=}YH_2$ compounds, where X = Ge or Sn and Y = C, Si, Ge, or Sn. These strengths are estimated both by evaluating the rotation barriers and by investigating the appropriate thermochemical cycles. The results show that C > Si $\sim$ Ge > Sn in their ability to form π-bonds.

I. Introduction

Recently there has been considerable interest in the molecular and electronic structure and the reactivity of compounds containing a double bond between group IVA elements. But, while the double bonds in ethylene, disilene, and silaethylene have been well-characterized by both experiment and theory (see, for instance, refs 1–5), the double bonds formed with germanium and tin have only recently been examined. Several reviews have been written on the subject of Ge and Sn double bonds.[6] Many of the species which contain double bonds to these elements are transient reactive intermediates. However, some have been isolated.

Through the use of large, bulky groups for steric and electronic stabilization, three germenes ($R_2Ge{=}CR'_2$) were isolated in 1987.[7,8] (Until then, germenes had been seen only as transient species.[9–12]) At that time, Berndt and co-workers[7] synthesized germenes **1a** and **1b**.



a, R = $N(SiMe_3)_2$

b, R, R = $NtBu(SiMe_2)NtBu$

1a,b

These stable germenes were characterized by both NMR and X-ray diffraction techniques. The Ge═C bond length was determined to be 1.827 Å, with an average twist angle of 36° about the GeC bond. In addition, the local structure about the Ge and

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