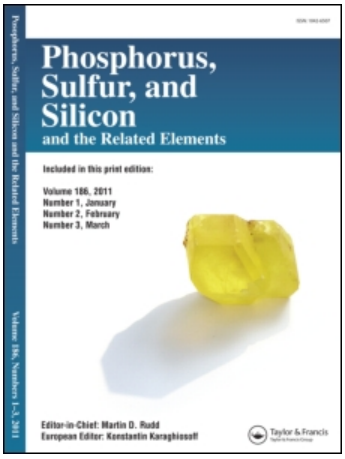

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Structural Rules of Phosphorus: Verification and Rationalization

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STRUCTURAL RULES OF PHOSPHORUS: VERIFICATION AND RATIONALIZATION

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Abstract The structural rules of phosphorus as formulated by Baudler and Häser apply to covalently linked networks of phosphorus atoms in the absence of perturbing factors. Here these rules are systematically verified by *ab initio* calculations, and justified in terms of more basic chemical concepts. Possible structures and conformers of the phosphanes P_3H_5, P_4H_6, P_5H_3, P_5H_5, P_5H_7, P_6H_6, P_8H_6, $P_{10}H_6$, $P_{13}H$, and $P_{13}H_3$ are discussed.

INTRODUCTION

The covalently linked networks of phosphorus atoms in (sterically or electronically unperturbed) polycyclic (alkyl)phosphanes, alkaliphosphides (with $P^-/P<1/5$), and allotropes of phosphorus (except the dense "black" forms) conform to the structural rules first outlined by Baudler[1,2] and subsequently refined by Häser[3,4]. The latter author speaks of PP covalency dominated structures. This work is intended as a critique of these structural rules. In particular, we will apply small changes to these rules, and subsequently test by *ab initio* calculations the stabilities of structures which are predicted by the changed rules, but not by the original rules. In other words we ask: How much energy is needed to violate the structural rules of phosphorus (as formulated in Ref.4). In addition, we justify the structural preferences of covalent phosphorus networks in terms of more basic chemical principles.

For lack of space we cannot reproduce here the rules, definitions and notations from Refs.3 and 4. We assume that the reader is familiar with these references. For later convenience we define as a *simple ring* any ring which does not have an internal zero-atom bridge. Examples of *non-simple rings* then comprise the four-membered rings in bicyclotetraphosphane and in tetrahedral P_4. The three-membered rings in the same molecules are simple rings.

1. ON RULE B1

Formal cycloadditions have been chosen as the major operations of structural aggregation. The wisdom of this choice will be questioned in Section 4 in context with rule B3. Given the formulation of rule B1 one is inclined to ask what additional structures result if in addition to formal 2+3 cycloadditions also n+m cycloadditions with $|n-2|+|m-3|=1$ are admitted. The condition $|n-2|+|m-3|=1$ means we consider "local" changes to rule B1. Two out of four possible choices for n,m lead to four-membered ring units. These will be discussed in Section 3. Only 3+3 and 2+4 cycloadditions are left.

The archetypical product obtained by a formal 3+3 or 2+4 cycloaddition is a six-membered ring of phosphorus. We recall that P_6H_6 has experimentally been found to be a phosphinocyclopentaphosphane rather than a cyclohexaphosphane.[2] Almost as surprisingly, *ab initio* SCF/SVP calculations indicate that the most stable isomer of cyclohexaphosphane is *not* the all-*trans* or *ttttt* isomer (the most stable conformer of which is a near-planar *chair* with all hydrogens in *axial* positions). This is counterintuitive in view of the energetic stabilities of the isomers and conformers of P_5H_5.[4] After extensive search we have found the *ctcctc* isomer of cyclohexaphosphane to be most stable (chair conformation with hydrogens oriented *exeexe; c=cis,t=trans,x=axial,e=equatorial*). The same conformation and substitution pattern of a P_6 ring is found in orthorhombic black phosphorus. The *eeeeee* substitution pattern of the *ttttt* P_6 rings in the rhombohedral form of black phosphorus does not correspond to a local minimum in the potential surface of P_6H_6 but rather relaxes to the *xxxxxx* conformer. The P_6H_6 conformers *exeexe* and *xxxxxx* are

calculated to be 21 and 31kJ/mol(P_6H_6) less stable than P_5H_5 at the SCF/SVP level of theory, respectively (zero point energies not included). If nuclear motion is accounted for in harmonic approximation, and entropy terms are evaluated for an ideal gas state, the standard free enthalpy of *exeexe* P_6H_6 can be evaluated as +38kJ/mol(P_6H_6) relative to the most stable isomer of P_5H_5. In line with these results, a single layer of orthorhombic black phosphorus is calculated (SCF/SVP level of theory) to be less stable than the tubular five-membered ring structures of Hittorf's phosphorus by about 20±10kJ/mol(P_4).[5] It must be concluded that it is electronic correlation which reverses the stabilities of red and black allotropes of phosphorus.

Formal 3+3 or 2+4 cycloadducts consistently turn out to be of inferior stability also in (poly)cyclic phosphanes other than P_6H_6, cf. Figs.1 and 2 where isomeric phosphanes P_8H_6 and $P_{10}H_6$ are compared.

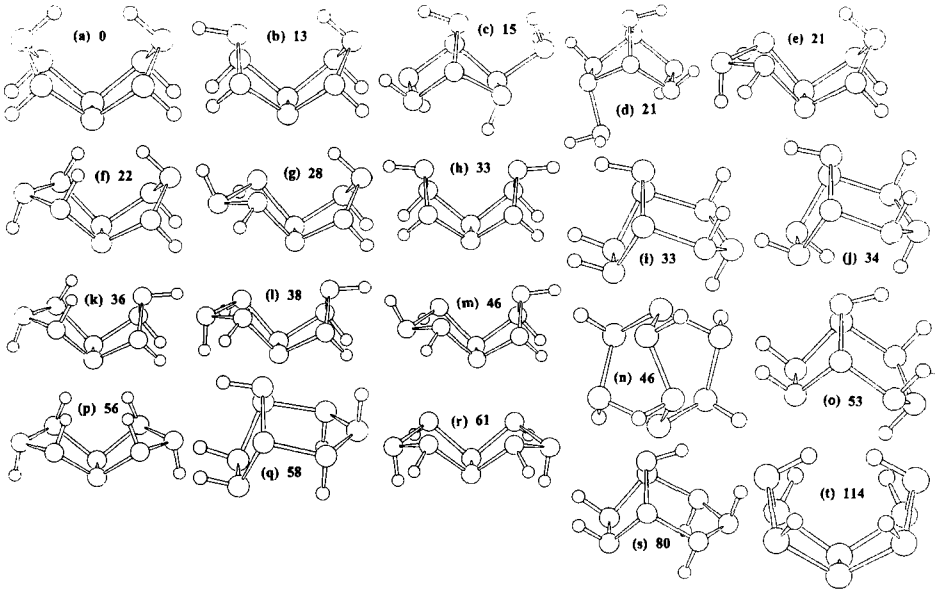

FIGURE 1 Representative isomers of P_8H_6 and their calculated (SCF/SVP) electronic energies (in kJ/mol) relative to the most stable isomer (a). Structures c and d have side-chains, Structure n may be addressed as 2+4 cycloadduct, and Structures i,j,o,q, and s are examples of 2+3 cycloadducts in which the P2 acceptor is a simple six-membered ring.

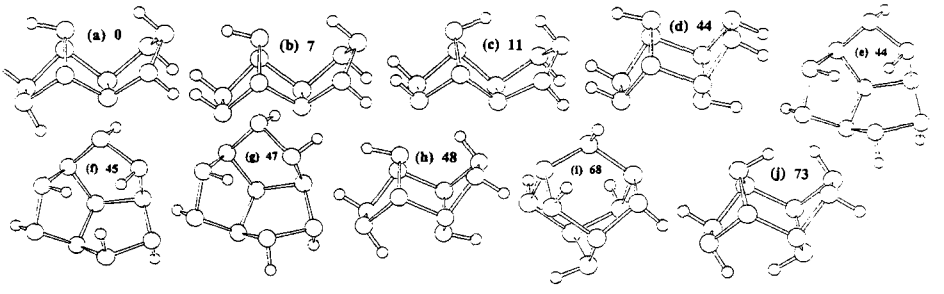

FIGURE 2 Representative isomers of $P_{10}H_6$ and their calculated (SCF/SVP) electronic energies (in kJ/mol) relative to the most stable isomer (a). Structures d, h, and j may be addressed as formal 3+3 cycloadducts of two five-membered rings; Structure i relates to adamantane, and Structures e, f, and g relate to perhydroquinacene.

Next let us consider violations of restriction B1R1. That polycylic phosphanes should not have terminal bonds is a *soft* rule in the sense that the energetic separation between phosphinopolycyclophosphanes and polycylophosphanes without side chains can be small (15kJ/mol in the case of P_8H_6, Fig.1a-d); experimental conditions are known under which polycyclic phosphorus structures with side chains can be obtained.[2] This point has also been recognized in Ref.4.

We turn to restriction B1R2. Against the rule let us add P2 onto a simple or non-simple six-membered ring. In the second case one obtains the non-Baudler structure depicted in Fig.3b. As a phosphane this structure is 52kJ/mol less stable than the isomeric Baudler structure shown in Fig.3a. This mode of concatenation can conclusively be dismissed.

From Fig.1 we conclude that 2+3 cycloaddition of a P2 unit onto a conformationally unrestricted six-membered ring yields isomers of P_8H_6 at least 30kJ/mol less stable than the most stable isomeric Baudler structure. Most of this energy difference may be attributed to using a non-Baudler structure as an educt, namely P_6H_6 which is less stable than P_5H_5 by at least 20kJ/mol. Indeed, if the most simple Baudler structure with a six-membered ring unit (P2[P3]P2) is employed as P2 acceptor (with the P2 unit added to the six-membered ring rather than to any of the the five-membered rings), the energetically rather competitive structure $(P2[P3]P2)]_6P2$ results. We refer the reader to Section 3.4 of Ref.4 where this structure and a corresponding extension of rule B1 have been discussed.

2. ON RULE B2

Rule B2 allows an introduction of zero- or one-atom bridges. Two-atom bridges may not be introduced by rule B2, and need not be discussed here as they are the subject of rule B1. Two restrictions constrain the introduction of zero- or one-atom bridges; the first of which (B2R1) states that simple four-membered rings may not be formed. This is equivalent to saying that 4+0 or 3+1 cycloadditions lead to polycyclic phosphorus structures of inherently inferior stability. 4+0 "cycloadditions" would indeed allow the construction of highly unstable structures like the polyhedral phosphorus analogues of cubane and prismane.[6,7] 3+1 cycloadditions will be discussed in Section 3.

We turn to restriction B2R2. Let us admit zero- or one-atom bridges which introduce rings of sizes 3 and 7 or 5 and 7, but none of the allowed combinations n,m<7.

Fig.3b shows the prototypical non-Baudler structure that results when a *zero*-atom bridge is introduced into a Baudler structure so that a three- and a seven-membered ring are formed. As mentioned before, this structure is much less stable (by 52kJ/mol) than the isomeric phosphane shown in Fig.3a, and the corresponding operation must be considered strongly forbidden. If two rings with sizes 3 and 7 are formed by adding a *one*-atom bridge to a Baudler structure, another Baudler structure will always be obtained. This operation is redundant.

Next we violate restriction B2R2 by introducing a *zero*-atom bridge into a Baudler structure so that a five-membered ring and a seven-membered ring results. The only Baudler structures P_n, n<13, which qualify as educts are Structures 29,40,41,48, and 57 from Scheme 2 of Ref.4. By inspection, only Structure 48 yields a promising product, and only if transannular strain in the resulting seven-membered ring can be alleviated by another one-atom bridge so that $P_{13}H_3$, Fig.3d, is obtained. This phosphane turns out to be of comparable energetic stability as isomers which relate to the Baudler structures P2[P8]P3(3), P7]P3]P3(3), and $P4(2)]_4P2[P5]P2$, shown in Figs.3c,e,f. $P_{13}H_3$ like $P_{13}H$ is experimentally known, but their structures are unknown.[2] $P_{13}H$ probably relates to $P4(2)]_4P2[P7$.

Finally consider a *one*-atom bridge added to a Baudler structure so that the ring sizes 5 and 7 arise. The only non-redundant case in question turns out to be a one-atom bridge added to the 2,7 positions of P3]P2[P3. The resulting structure, $(P2[P3]P2)]_6P2$, i.e. Structure 59 in Scheme 3 of Ref.4, can also be constructed by admission of 2+3 cycloadditions of P2 onto simple six-membered rings, see above and also Section 3.4 of Ref.4.

3. ON RULE F

Undisturbed polycyclic polyphosphorus structures containing simple four-membered ring units usually tend to be less stable than isomeric Baudler structures. Repulsion between parallel σ bonds[8,9] and/or electronic correlation effects[4] have been blamed for the instability of simple four-membered ring units. The motivations for admitting simple four-membered ring units (extended Baudler set $b0_F$) and calculated stabilities of some resulting structures have been given elsewhere.[3,4] Here we focus on a technical point: Should simple four-membered ring units be constructed by 2+2 cycloadditions as formulated in rule F, or

shoud one use (instead or as well) 3+1 cycloadditions (i.e. drop restriction B2R1)? Both approaches have their shortcomings. As a weakness of rule F note bicyclo[2.2.0]hexaphosphane and its higher homologues $P_{2n+4}H_4$, n>0. These structures are certainly superfluous since more stable isomeric Baudler structures, e.g. P3]P3(3), exist. The annealed four-membered ring structures $P_{2n+4}H_4$ cannot be constructed if we switch from 2+2 to 3+1 cycloadditions. The other way round we may ask which structures can be generated by 3+1 additions, but not by rule F. In this class we find structures with bridgeheads which belong to three four-membered rings; the phosphane structure depicted in Fig.3h is the archetypical example. At the SCF/SVP level of description this phoshane is less stable by 29kJ/mol than the isomeric P_5H_3 structure depicted in Fig.3g (P_5H_3 may also be a five-membered ring with a PP double bond not to be discussed here). Tetracyclo[3.2.0.$0^{2,4}$.$0^{3,6}$]heptaphosphane is another structure with bridgeheads belonging to three four-membered ring units; this structure resembles the least stable isomer of P_7H, if one counts only species without double bonds.[3] At this point 2+2 cycloadditions as a practical tool to generate structure proposals for phosphorus clusters or hydrogen-poor phosphanes appear to be a reasonable choice.

Structures with bridgeheads that belong to two or more simple four-membered rings can be avoided altogether, if the simple four-membered ring unit P4(4) is introduced as additional basic structure unit, and rule F is discarded. While this removes a large number of insignificant structures from the set $b0_F$,[4] the most stable cluster structures P_8 [6] and P_{12} [10] would be lost as well.

4. ON RULE B3 AND THE STABILITY OF FIVE-MEMBERED RINGS

In their essence, and without their restrictions, rules B1 and B2 comprise *all* possibilities to form five-membered rings (i.e. by 2+3, 4+1, or 5+0 operations). Other ring sizes are usually formed only in company with five-membered rings (rule B2 admits a small number of other ring combinations to be introduced in—as it turns out[4]—a limited number of cases). In addition to the five-membered ring generating rules B1 and B2, the central role of five-membered rings in phosphorus chemistry is highlighted by the Baudler index rule,[3,4] which is based on Baudler's rule of the maximum number of five-membered rings.[2] Rule B3 finally states that two Baudler structures may be linked by a single bond (without ring closure), if their concatenation by 2+3 cycloaddition is not possible.[4] Extensive *ab initio* calculations have shown that hypothetic macromolecules of elementary phosphorus built from small Baudler structures by such single bond links are of inferior stability when compared to corresponding polymeric Baudler structures or their networks.[4]

Despite such computational evidence, and despite the overwhelming empirical evidence for the predominance of five-membered rings in the structural chemistry of phosphorus,[2,11] one would like to see a more direct and quantitative verification of the higher intrinsic stability of phosphorus five-membered rings as compared to linear structures. Fig.3i-l shows the presumably most stable conformers of the linear phosphanes P_nH_{n+2} for 2<n<6. Their structures are characterized by a *gauche* conformation of all PP bonds, by the avoidance of a parallel orientation of lone pairs in 1,3 positions, and by PPPP torsional angles near 180 degrees (to avoid non-bonding interactions between groups in 1,4 or 1,5 positions).

If one compares the energy of cylcopentaphosphane P_5H_5 (*tttte* isomer and *xxxxx* conformer[4]) to the energy increments per PH group obtained from the most stable linear phosphanes P_nH_{n+2} and $P_{n-1}H_{n+1}$, one finds the five-membered ring to be more stable by 9, 2, and 12kJ/mol(P_5H_5) for n=5,4, and 3, respectively. The corresponding numbers with respect to the *anti* conformers of the linear phosphanes are 26, 26, and 29kJ/mol(P_5H_5). The differences indicates that a single PH group in a linear phosphane with all PP bonds in *anti* conformation is between 3.5 and 5 kJ/mol(PH) less stable than in the optimal *gauche* conformation. This *gauche* effect[12] has extensively been discussed with respect to diphosphane.[13] Since the *xxxxx* conformer of P_5H_5 has four PP bonds in a *gauche* conformation, and avoids 1,3 lone pair interactions (in other words: all lone pairs are in equatorial positions[4]), its small ring strain appears well understood. However, *xxxxx* P_5H_5 suffers from one eclipsed PP bond while in this work we have confirmed the earlier observation[14] that its ring strain may even be *negative*. Some *weak* electronic effect may be suspected to additionally stabilize the five-membered ring, but this will not be discussed here.

The *xxxxxx* conformer of cyclohexaphosphane needs to adopt its near-planar ring geometry (calc. PPP bond angle: 118.6°) *not* to avoid steric interactions between hydrogen atoms in 1,3 positions (their distances are 365pm which is substantially larger than trans-annular HH distances in *xxxxx* P_5H_5: 324pm and 345pm), but to avoid the near-parallel orientation of the equatorial lone pairs that would arise in a more puckered ring. The comparatively low stability of *xxxxxx* cyclohexaphosphane thus is explained. The large bond angle strain in cyclohexaphosphanes can be avoided, if lone pairs occupy axial positions, usually at the expense of transannular 1,3 lone pair interactions (which are smaller in magnitude than in

five-membered rings[15]) or at the expense of PP bonds in *anti* conformation. This applies to the two most stable *chair* conformers: *exeexe* and *xexexe* (this is the all-*cis* substituted ring!). Even some *boat* and *twist* conformers of cyclohexaphosphane are more stable than the *xxxxxx chair*.

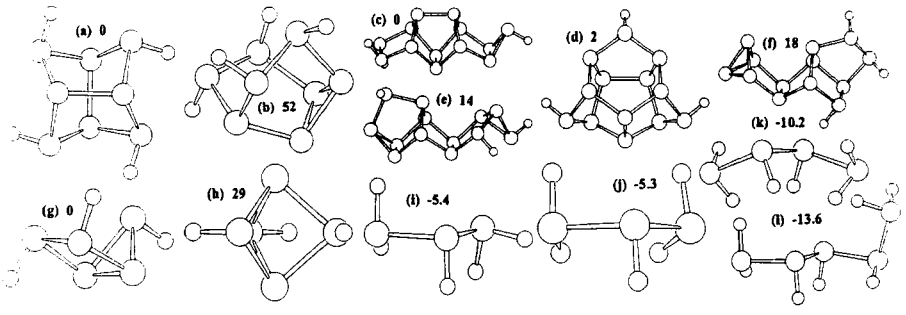

FIGURE 3 Selected phosphane structures P_8H_4 (a-b), $P_{13}H_3$ (c-f), P_5H_3 (g-h), and the most stable conformers of the linear phosphanes P_nH_{n+2} for $2<n<6$ (for n=4 an extensive search of the global minimum has been performed, but for n=5 only isomers which originate from structure k by replacement of H by PH_2 have been considered). Calculated (SCF/SVP) relative energies are given in kJ/mol relative to the most stable isomer depicted, or (in case of the linear phosphanes) relative to the respective all-*anti* conformers (not shown). The underlying common structural principles are nicely exhibited by the similarity of conformations, compare e.g. Fig.3k and Fig.1a.

CONCLUSION

The structural rules of phosphorus first outlined by Baudler[1,2] and subsequently refined by Häser[3,4] have been confirmed by systematic *ab initio* calculations. Some borderline cases, e.g. structures with side chains or with certain seven-membered rings, have been noted before and may be covered by suitable extensions of the rules.[4] The outstanding stability of cyclopentaphosphane has been explained by the *gauche* effect[12] and by the absence of 1,3 lone pair interactions; a further stabilization of P_5H_5 by *weak* electronic effects is likely. In general, five-membered rings produced by formal 2+3 cycloaddition display similarly preferred conformations as unconstrained P_5H_5. This justifies the rules B1 and B3 in terms of more basic chemical principles. Rule B2 has already been rationalized in Section 3.1 of Ref.4.

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