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Communications to the Editor

Structural Rules of Phosphorus

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Starting from earlier work by v. Schnering[1] and Baudler,[2-4] we introduce a chemical heuristic for the systematic deduction and classification of covalent partial structures of phosphorus in polycyclic phosphanes,[4] extendable also to other PP covalency dominated structures,[4,5] including the allotropes of phosphorus except the black forms.[5,6]

As is well-known,[4,5] phosphorus forms up to three PP bonds with bond lengths and bond angles varying from 215 to 230 pm and from 60° to 120°, respectively. Among the structural manifold available under this premise, covalent phosphorus partial structures in typical polyphosphorus compounds prefer only a relatively small subset of characteristic structures.[4,5]

Baudler's rules[2-4] establish clear relationships among most phosphane structures, partially including the covalent phosphorus linkage in Hittorf's phosphorus and in some polyphosphides. Yet there are deficiencies. Two highly condensed phosphanes ($P_{11}H_3$ and $P_{14}H_4$) cannot be *directly* related to the other known phosphanes and need to be addressed as "particular, compact structures which are energetically favoured".[4] While the P_{11} skeleton of $P_{11}H_3$ fits Baudler's rule of "the maximum number of five-membered ring units",[4] the same rule would predict dodecahedral P_{20} to be rather stable, in contradiction to recent ab initio results.[7] According to Baudler,[4] seven-membered rings will not be incorporated into phosphane structures, but this is *formally* at odds with the *hidden* occurrence of such rings in the rather stable P_9 cages that can be found in Hittorf's phosphorus[6] and many phosphanes.[4] In this communication we suggest a modification of Baudler's rules which does not suffer from the aforementioned shortcomings.

Let us define as *basic structure units* the diphosphane unit P2, i.e., two P atoms linked through a single bond with four free valences left, and the acyclic triphosphane unit P3 with five free valences. We further define as *Baudler structures* those two basic structure units and additionally all covalent structures which can be assembled by successive application of either of the following two rules, B1 and B2, subject to the aforementioned restrictions on bond lengths, bond angles, and the connectivity of phosphorus.

B1. Rule of Aggregation. Formal 2 + 3 cycloaddition of a basic structure unit to a Baudler structure yields a larger Baudler structure. The following restrictions apply:

B1R1. The product must not have terminal atoms.

B1R2. Addition of P2 to two nonterminal atoms is allowed *only* if the reacting three-atom sequence is part of a four- or five-membered ring.

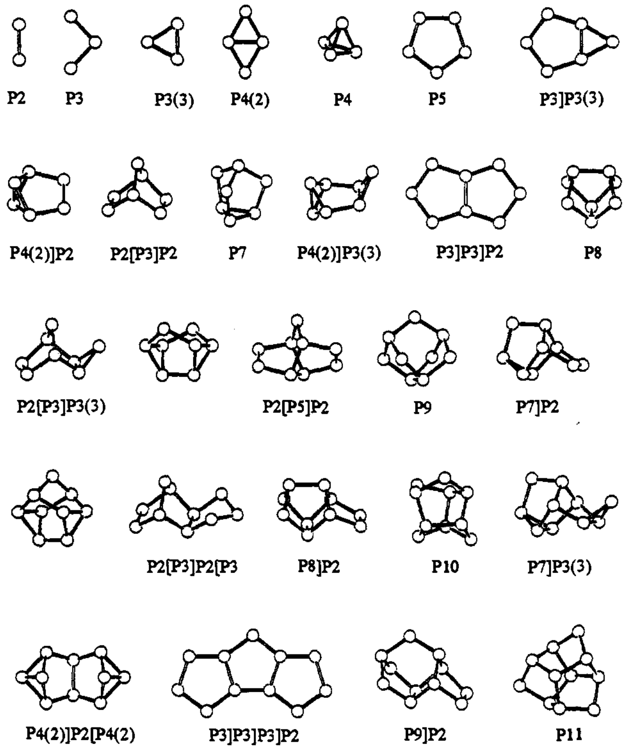

Figure 1. Covalent structures of phosphorus constructed from rules B1 and B2 (Baudler structures).

B2. Rule of Condensation. Zero- or one-atom bridges may formally be introduced subject to the following restrictions.

B2R1. A newly formed bridge may not be part of a four-membered ring that has no internal bonds.

B2R2. In polycyclic products there exist two rings with sizes <7 which share the newly formed bridge but do not have any other atoms in common.

In line with Baudler's rule[4] of "the maximum number of five-membered ring units" we further define for each Baudler structure a *Baudler index* as the difference between the number of five-membered rings and the number of three-membered rings.

When rules B1 and B2 are applied to generate all Baudler structures, one will find *all* structurally known polycyclic phosphanes, including $P_{11}H_3$, $P_{14}H_4$, and even P_4. One will *not* find dodecahedral P_{20}. A limited number of unknown structures will be generated all along, but among isomeric Baudler structures those with the highest Baudler indices are almost in a one-to-one correspondence with experimentally known polycyclic phosphanes and related compounds.

For clarification consider all Baudler structures up to P_{11}. Using paper, pencil, and rules B1 and B2, a total of 47 such structures can be found. Twenty-three of these structures may tentatively be discarded as they are isomeric to Baudler structures with higher Baudler indices. The remaining 24 Baudler structures are depicted in Figure 1, where we also included three Baudler structures, labeled P2[P3]P3(3), P9, and P10, that rank second in Baudler index with respect to their isomers P8, P2[P5]P2, and P8]P2, respectively.

The following structures in Figure 1 are known from phosphanes:[4] P2, P3, P3(3), P4(2), P5, P3]P3(3), P4(2)]P2, P2[P3]P2, P7, P3]P3]P2, P8, P2[P3]P3(3), P2[P5]P2, P9, P7]P2, P2[P3]P2[P3, P8]P2, P9]P2, and P11. This includes all structurally known polycyclic phosphanes up to $P_{11}H_m$.[4] Of the other structures in Figure 1, P4 constitutes white phosphorus,

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P10 is a substructure within $P_{14}H_4$,[4] and P4(2)]P2[P4(2) is the smallest phosphorus cluster calculated to have an energetic stability comparable to that of tetrahedral P_4.[7] P4(2)]P3(3), P7]P3(3), and P3]P3]P3]P2 may be expected to relate to the known, yet structurally uncharacterized phosphanes P_7H, $P_{10}H_2$, and $P_{11}H_7$.

In the case of $P_{10}H_2$ this prediction is confirmed by ab initio MP2fc/SVP//SCF/SVP calculations:[8] a previously favored structure proposal[4] (pentacyclo[4.4.0.0^{2,8}.0^{3,5}.0^{4,7}]decaphosphane, which contains a four-membered ring) is calculated to be higher in energy by 10 kJ/mol when compared to the hydride of P7]-P3(3).

The structure of P_7H has previously been predicted to correspond to P4(2)]P3(3).[4] The set of all geometrically possible structures P_7H without PP double bonds consists of two stereoisomers of tetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptaphosphane (the *trans* isomer will be designated P4(2)]P3(3)-H), two stereoisomers of tetracyclo[3.2.0.0^{2,4}.0^{3,6}]heptaphosphane, and one stereoisomer of tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptaphosphane (here labeled P7(1)-H). On the basis of ab initio SCF/SVP[8] structure optimizations, two isomers, P4(2)]P3(3)-H and P7(1)-H, turn out to be isoenergetic to within 3 kJ/mol whereas the rest are higher in energy by at least 25 kJ/mol. MP2/SVP[8] structure optimizations, coupled cluster CCSD(T)fc/SVP//MP2/SVP[8] single point energies, and large basis set MP2/TZV′2d1f structure optimizations all predict P4(2)]P3(3)-H and P7(1)-H to be about isoenergetic. Free energies of P4(2)]P3(3)-H and P7(1)-H calculated from vibrational and rotational partition sums (using harmonic SCF/SVP frequencies and SCF/SVP equilibrium structures) indicate the former isomer to be favored entropically by as little as 1.5 kJ/mol when going from 0 to 500 K.

We note that species with four-membered rings as in P7(1)-H can be systematically derived, too, if in addition to the operations in rules B1 and B2 formal 2 + 2 cycloadditions are admitted. The additional structures that can be generated in this way usually are energetically less favorable and need to be considered only if no isomeric Baudler structure with a favorable Baudler index can be found. This applies, in part, to P_7H, presumably to P_8H_2, and to many uncharged phosphorus clusters studied by theoretical approaches.[7,16]

As the reader may have noticed, the symbols [and] in labels like P7]P2 indicate a concatenation—here of P7 with P2—via formal 2 + 3 cycloaddition. Note the asymmetry: P2[P7 and P7]P2 denote the same 2 + 3 or 3 + 2 cycloadduct, but P7[P2 would not be possible. By this notation one can constitutionally characterize and symbolically derive *all* Baudler structures comprising more than 12 P atoms.[17] Only the structurally known, higher phosphanes shall be listed here: P2[P8]P2, P2[P9]P2, P9]P2[P3, P2[P10]P2, P7]P2[P7, P9]P2[P5]P2, P9]P2[P7, P2-[P9]P2[P5]P2, and P9]P2[P9 characterize $P_{12}H_4$, $P_{13}H_5$, $P_{14}H_6$, $P_{14}H_4$, $P_{16}H_2$, $P_{18}H_6$, $P_{18}H_4$, and two isomers of $P_{20}H_6$, respectively.[4] The same phosphorus partial structures also constitute substituted polycyclic phosphanes[4] unless sterically or electronically disturbing substituents force the occurrence of phosphorus partial structures that would otherwise be unstable.

Of the polymeric Baudler structures possible, those with the repeating units]P2[P5],]P2[P3]P2[P8], and]P2[P9]P2[P8] are experimentally known from LiP_7, LiP_{15}, and Hittorf's phosphorus, respectively.[5] Guided by rules B1 and B2, and allowing for cross-links between the so-constructed (finite or polymeric) Baudler structures, it becomes possible to direct ab initio methods in the quest for structural alternatives to the only red allotrope of phosphorus that has been structurally characterized (Hittorf's phosphorus[6]). Full details will be given elsewhere.[18]

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(8) The acronyms SCF, MP2, and CCSD(T) refer to the self-consistent field method,[9] second-order Møller–Plesset (many-body) perturbation theory,[9] and the coupled-cluster method with a perturbative treatment of triple excitations;[10,11] "fc" stands for the frozen-core approximation, i.e., omission of core electrons from correlation treatments. The acronym SVP refers to a split valence (SV) basis set[12] augmented by one set of (five) d functions at phosphorus (orbital exponent $\zeta_d = 0.45$) and one set of p functions at hydrogen ($\zeta_p = 0.8$). TZV′2d1f labels a basis set of triple ζ valence quality (TZV′)[13] at phosphorus, augmented by two d shells and one f shell ($\zeta_d = 0.70, 0.25$; $\zeta_f = 0.46$), and used in conjunction with the SVP basis set at hydrogen. The rest of the nomenclature follows suggestions from ref 9. SCF and MP2 structure optimizations have been carried out with the program system TURBOMOLE.[14] CCSD(T) calculations have been performed with the program system ACES II.[15]

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(17) The largest Baudler structure that cannot be decomposed in terms of A]B (i.e., by formal 2 + 3 retrocycloaddition) contains 12 P atoms. The avoidance of corresponding larger cages like dodecahedral P_{20} is an indirect consequence of restriction B2R2 and is physically rooted in unfavorable near-planar coordination of phosphorus in large cages.

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