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Dedicated to Professor Ionel Haiduc,
President of The Romanian Academy at his 70th anniversary

SECONDARY INTERACTIONS IN HETEROALLENIC SYSTEMS WITH P=C-E UNITS

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ABSTRACT. Intermolecular interactions of -CH···O, -CH···HC- -CH···F and –CH···π types are responsible for the building of the crystal structure of *bis*-(phosphane oxide)methylene **3**, phosphinic acid derivative **4** and arsanyl-*bis*-(methylene)-phosphorane (**5**) as chains and layers.

Keywords: heteroallenes, intermolecular contacts, heterocumulenes, arsanylbis(methylene)phosphorane

Introduction

Heteroallenic and heterocumulenic derivatives containing a group 14 and 15 heavy element have been in attention in the last years due to the novelty of the ways of the stabilization of the double bonds established between heavy elements [1, 2]. However the interest on such systems has been focused mainly on the core of the molecule and little attention has been paid on the role of the voluminous substituents - other than that of allowing for enough steric protection.

Substituted derivatives containing the Mes*P=C unit (Mes* = 2, 4, 6-tri-*tert*-butylphenyl) are of interest as precursors of phosphacumulenes of the type P=C=E and E'=P=C=E (E, E' = group 14 and 15 element), due to the steric protection afforded by the bulky supermesityl group [3]. In this respect, compound **1**, and **2** [4] bearing the sterically demanding substituents at phosphorus and at phosphorus and arsenic in **3** [5] have been synthesized and fully characterized in solid state by a single crystal X-ray diffraction. **1,** which is the first diphosphaallene featuring a $\lambda^5\sigma^3$ and a $\lambda^3\sigma^2$ phosphorus atom, the phosphavinylidene(oxo)phosphorane Mes*P(O)=C=PMes* (Mes* = 2,4,6-tri-*tert*-butylphenyl) has been synthesized in a one pot procedure starting from Mes*P=C(Cl)Li which reacts with Mes*P(O)Cl_2 [4]. The stabilizing effect of the substituents is revealed by the fact that **1** is stable for months at room temperature in the solid state but slowly rearranged in solution (about one day in THF and two days in pentane, toluene or chloroform) to afford in

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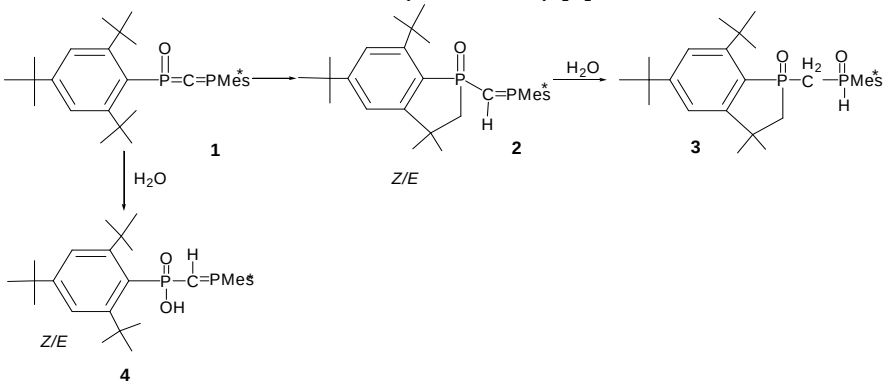
near quantitative yield the phosphaalkenylphosphine oxide **2** in the form of two *Z/E* isomers in the ratio 85/15 (Scheme 1) [4].



Scheme 1

By addition of the difluoroarsane Mes*AsF_2 to the supermesityl[bis(trimethylsilyl)methylene](lithiochloro-methylene)phosphorane, the first arsanylbis(methylene)phosphorane, $(Me_3Si)_2C=P(Mes^*)=C(Cl)$-As(F)Mes* **5** (Mes* = 2,4,6-tri-*tert*-butylphenyl) has been synthesized [5].

The structures of **3, 4** and **5,** unambiguously established by single crystal X-ray diffraction study, displays classical bond lengths and angles.

In this paper we discuss some secondary interactions leading to supramolecular associations shown by the crystal structures of **3**, **4** and **5**.

Results and discussion

Two (P=)O···H(Ar) intermolecular contacts are responsible for packing of **3** in chains (along the a axis) through the short bifurcated hydrogen bonds (Figure 1) of 2.65 Å (from O1 to H(Ar)) and 2.52 Å (from O1 to one of the methyl groups substituting the phospholene ring).

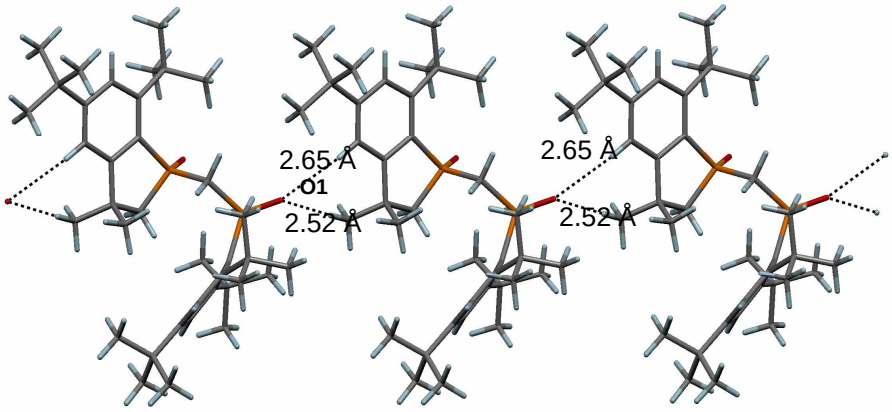


Figure 1. Crystal structure of 3 showing the short intermolecular contacts

Such intermolecular P=O···H(C) contacts are quite common in the chemistry of organophosphorus (V) systems, and the Cambridge Data Base search displays 1484 from the total of 400977 entries registered in January 2007. [6]

Due to the presence of P(O)OH groups, **4** displays in the crystal structure dimeric units formed through O···H contacts of 1.79 Å.

The O···O distances are of 2.564 Å, not very different from those found in bis(*p*-methylphenyl)-phosphoric acid dimer O···O 2.512 [7] or tetrakis(methylguanidinium) monohydrogen orthophosphate O···O 2.503 Å, 2.545 Å [8] showing that the overall organic environment of phosphorus does not change the properties of this fundamental unit (Figure 2).

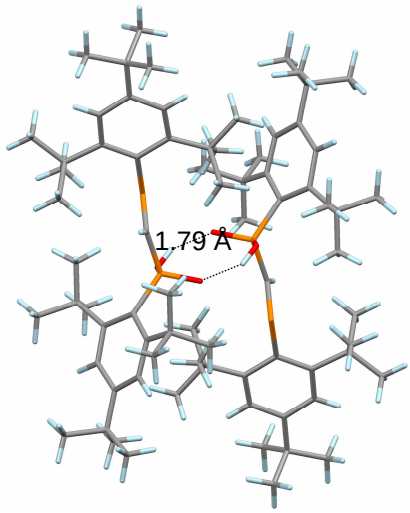


Figure 2. Dimeric units formed by short OHO contacts in the crystal structure of 4.

These dimeric units exhibit further CH···HC contacts (of 2.38 Å) between the *o* H-Mes* groups of neighbouring fragments leading to chair like polycicles (one is highligthed by CPK representation in Figure 3) displaying cavities of 5.6-5.8 Å diameter.

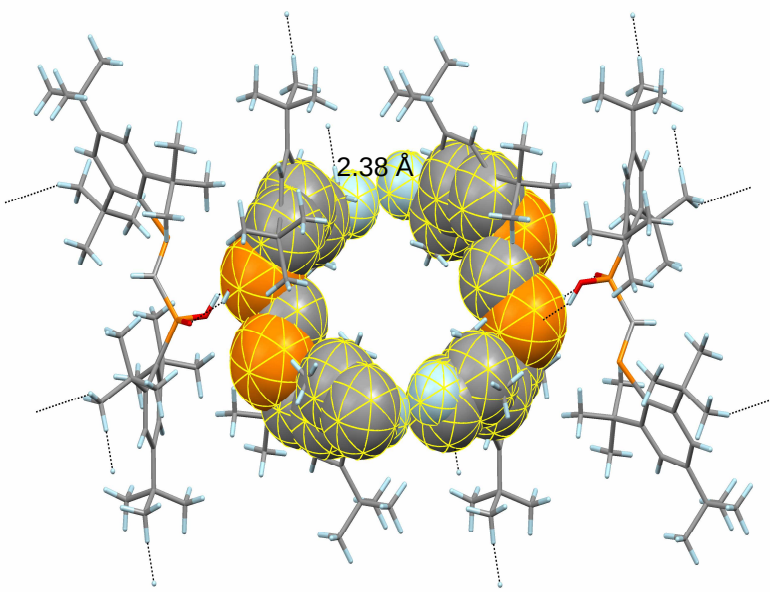


Figure 3. The chain arrangement of 4 is shown, highlighting the short HH contacts.

Close H···H contacts (2.289 Å) are also displayed in a 9-trimethylsilyl substituted fluorene derivative of germatrane [9] a finding which might be relevant in view of the increased interest paid in the last years to such interactions [10-13]. However, a systematic search in the Cambridge Database reveals that –CH···HC- contacts shorter than the sum of the van der Waals radii are quite common (we found 2051 entries from a set of 400977 data [6].

The *p* H Mes* groups of **4** come also close, so that finally a layer is formed as shown in Figure 4,. Neighbouring cycles are in contact within distances of 2.32 Å (Figure 4) which are still shoter than the sum of the van der Waals radii of hydrogen (2.40 Å, [14]).

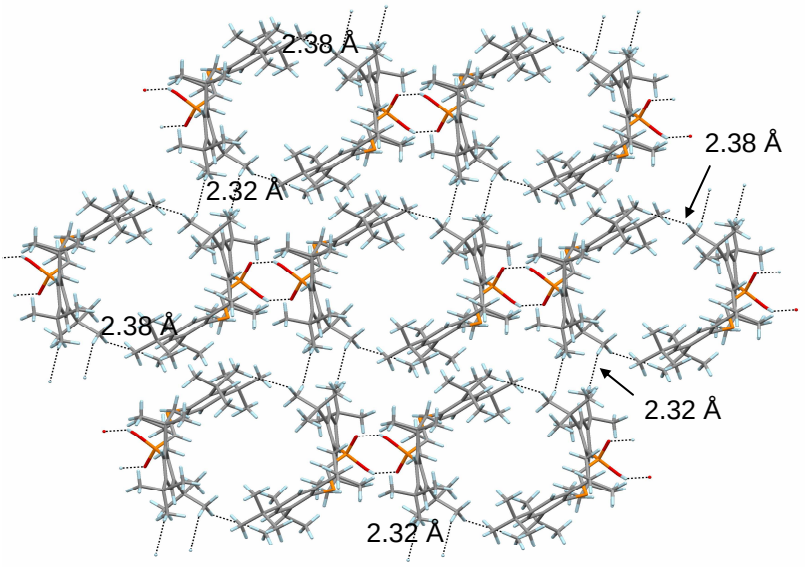


Figure 4. A top view of a layer formed by chair-like rings in 4

In the case of arsanylbis(methylene)phosphorane $(Me_3Si)_2C=P(Mes^*)=C(Cl)-As(F)Mes^*$ **5,** the main interactions in the crystal packing are the H···F bonds (2.59 Å) between the hydrogen atom from a Mes* and the fluorine from a neighbouring molecule leading to dimeric units (Figure 5). These dimers are supported also by CH···π (2.97 Å) interactions between the H of one Mes* fragment and the aromatic ring from neighbour Mes* (Figure 5).

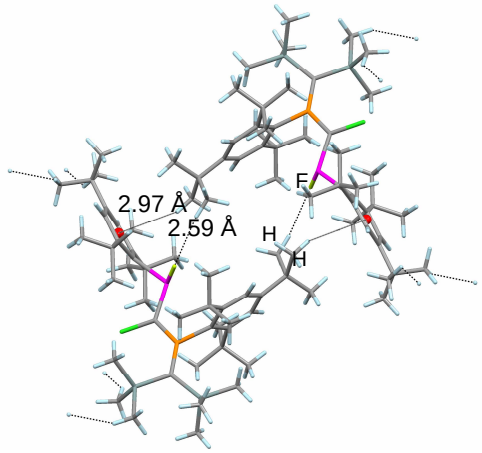


Figure 5. Dimeric units formed by CH π contacts found in the crystal structure of 5

Further, the dimers are connected through H···H contacts (2.33 Å) and a zig-zag type chain is formed (Figure 6 **a**). These chains form a layer through H···H secondary interactions (2.36 Å), brought by the *t*-Bu groups of the supermesityl radicals (Figure 6 **b**).

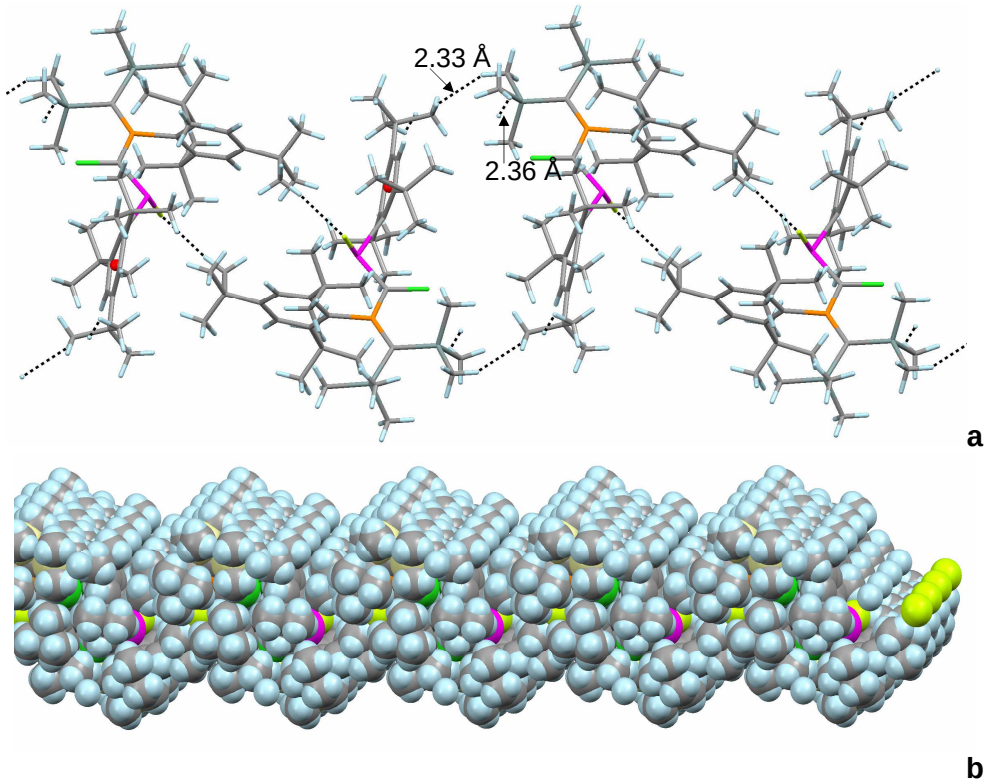


Figure 6. The crystal structure of 5 showing the chain arrangement (a) and the extension of these chains in a layer (b)

Conclusion

The voluminous substituents on the phosphallenic fragments responsible for the kinetic stabilization of the phosphorus carbon double bonds have also certain effects on the packing in the crystal structure and determine the formation of interesting supramolecular frameworks.

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