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Theoretical study of structural patterns in CH₂OP₂ isomers

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Abstract

DFT calculations have been performed on the derivatives of formula CH₂OP₂ to determine their total energy, the relative energy between the isomers and their geometry. Among compounds with a P-C-P linkage, the most stable one is the 2-hydroxy-1,2-diphosphirene **II.1**, a three-membered heterocycle with a P=C unsaturation. The phosphavinylidene(oxo)phosphorane HP=C=P(O)H **IV.5** (which has the same skeleton as the experimentally obtained Mes*P=C=P(O)Mes*) lies 36.30 kcal mol⁻¹ above it. The least stable compounds are carbenes; the singlet carbenes are more stable than the triplet ones.

Keywords Phosphavinylidene(oxo)phosphorane isomers · DFT calculations · NBO analysis · Heteroallenes

Introduction

The geometric and electronic structure of various types of phosphorus compounds is now well known. In the field of doubly-bonded compounds, it is the case of phosphalkenes -P=C< which have been intensely studied [1].

For phosphorus derivatives which possess two cumulated double bonds, such as heteroallenic derivatives -P=C=E ($\text{E} = \text{C}, \text{N}, \text{P}, \text{O}$) [2], *ab initio* calculations have been reported on the parent 1,3-diphosphaallene HP=C=PH , on several XP=C=PX ($\text{X} = \text{H}, \text{F}, \text{Cl}$) models [3, 4], on azaphosphaallene HP=C=NH , [3, 5] and on phosphaketene HP=C=O [6]. The results on the geometries, the substituents' effect on the stability of these heteroallenes and their isomers, their configurational stability, their electronic structure and several other molecular properties have been studied and compared to those of phosphalkenes -P=C< and also to carbodiimides -N=C=N- .

We have been interested in the synthesis, characterization and reactivity of a new type of diphosphaallenes and have reported the synthesis and characterization of the phosphavinylidene(oxo)phosphorane $\text{Mes}^*\text{P=C=P(O)Mes}^*$ ($\text{Mes}^* = 2,4,6\text{-tri-}t\text{-butylphenyl}$), the first diphosphaallene containing both $\lambda^3\sigma^2$ and $\lambda^5\sigma^3$ phosphorus atoms [7]. Such system offers potential use as transition metal ligands and elucidation of its electronic structure should provide insight in the nature of heteroallenic compounds, leading to the design of better synthetic routes. The presence of two phosphorus atoms in a molecule with different bonding to carbon or oxygen atoms might induce electronic effects influencing the structural parameters and stability of such derivatives.

This paper reports density functional theory (DFT) calculations on the HP=C=P(O)H model and its isomers of the general formula CH_2OP_2 in order to determine the most stable systems and thus most likely to be experimentally obtained. The main geometrical parameters of all these derivatives are also reported. Although calculations have been performed on all the possible isomers, we limit our presentation to cyclic and acyclic derivatives with a P-C-P linkage.

Methods

Starting structures were built with GaussView 4.1 [8]. Geometries were optimized using the Gaussian 09 software package [9], at the B3LYP/6-311++G(d,p) level of theory using the default convergence criteria. Single-point calculations were also performed using high-correlation (CCSD/SDQ/6-31G*) and Moeller-Plesset (MP4/6-31G*) methods in order to see if the results are in agreement with the DFT data. Vibrational analyses confirmed that all geometries shown here represent true minima.

Results and discussion

Depending on the skeleton, the results have been grouped in different series: cyclic series with four-membered rings (**I**), two series containing three-membered rings (a PPC cycle (**II**) and a PCO cycle (**III**)), and a non-cyclic series with a PCP skeleton (**IV**) (Scheme 1). We have long been interested in the field of heteroallenes of the type $P=C=E$, particularly 1,3-diphosphaallenic compounds [2, 7]; thus, the current discussion will be focused on derivatives containing the P-C-P unit. All of the other possible isomers were also found, but this discussion will only refer to cyclic or non-cyclic structures built starting from the above mentioned moiety. Where several conformers were identified, only the most stable of them is reported. The isomers studied include doubly- or triply-bonded derivatives as well as carbenes.

<Scheme 1>

Fig. 1 presents the relative energies of all of the investigated structures optimized with DFT method. The optimized structures of the isomers are presented in Table 1 together with relevant geometrical data.

<Figure 1>

<Table 1>

The most stable of all the possible isomers with a P-C-P linkage was found to be the three-membered heterocycle 2-hydroxy-1,2-diphosphirene **II.1** (Table 1). Thus, energies of all the isomers discussed in this paper are given relative to its total energy. Fig. 1 is instructive from an experimental point of view, as it illustrates 7 structures within ~ 10 kcal mol⁻¹ of the reference energy, suggesting a wide variety of isomers may be accessible experimentally and very close in energy to each other, which offers promise but also warns of difficulties in isolating pure compounds in good yields. However, substitution with bulky groups at both P1 and P2 should have an important effect on the stabilization of these derivatives and should thus allow a better control of the synthetic route towards the desired target.

In the four-membered ring series, the most stable isomer is the 2*H*-1,2,4-oxadiphosphete (**I.1**) with a relative energy of 4.74 kcal mol⁻¹ in relation to **II.1**. Three-membered heterocycles with a PCO ring skeleton are calculated to be less stable than the ones with a PPC ring (for example 29.33 kcal mol⁻¹ for **III.1**).

In the case of open-chain structures, the most stable compounds are **IV.1** and **IV.2** (*Z*, *E* isomers of HP=CH-P=O), followed by the phosphaacetylenic derivatives **IV.3** and **IV.4** (7.83 and 15.09 kcal mol⁻¹, respectively) and the phosphavinylidene(oxo)phosphorane **IV.5** (36.30 kcal mol⁻¹). For all the series investigated, the carbenoid structures are the most unstable isomers (generally 45 to 84 kcal mol⁻¹ higher in energy than the three-membered ring derivative **II.1**).

Singlet structures were calculated to be more stable than the triplet ones. For example **I.4** was calculated to be 12.98 kcal mol⁻¹ more stable than **I.5** (with the hydrogen atoms in a *trans* position relative to the four-membered ring). For the *cis*-structures (investigated, but not shown in Table 1, the difference is somewhat smaller (around 7 kcal mol⁻¹)).

A model of the bis(supermesityl)phosphavinylidene(oxo)phosphorane Mes*P=C=P(O)Mes* (Mes* = 2,4,6-tri-*tert*-butylphenyl) [7], shown experimentally to be stable at room temperature, is found among those shown in Table 4 - HP=C=P(O)H **IV.5**, - and is not among the most stable CH₂OP₂ derivatives. In principle, there are several possibilities whereby Mes*P=C=P(O)Mes* could rearrange to structures predicted more stable in Table 1: by a cyclization of the C=P=O unit (to lead to the structures of the type **III.1**), by a migration of the organic group from a phosphorus to the adjacent carbon atom (to form analogues of **IV.1** or **IV.2**), or by migration of the substituent to the second phosphorus or the oxygen atoms (to form phosphaacetylenic

compounds like **IV.3** and **IV.4**). All the resulting structures are calculated to be more stable in the case of the model compounds. The stability of the diphosphaallene $\text{Mes}^*\text{P}=\text{C}=\text{P}(\text{O})\text{Mes}^*$ is probably due to steric reasons. For instance, in a structure of the type **IV.1** and **IV.2**, the presence of two extremely bulky supermesityl groups on adjacent atoms (P and C) is unlikely, as well as a very hindering group on the central carbon atom. The fact that phosphaacetylenic derivatives were calculated to be among the most stable structures is not surprising since phosphaalynes $\text{RC}\equiv\text{P}$ are well known [10], and their stabilization is possible even in the absence of a bulky group such as a supermesityl.

Ab initio calculations (HF/4-31G and HF/DZP-11s7p2d/6s4p2d for the P atom) performed on models with the CH_2P_2 formula placed a diphosphirene structure (a three-membered ring with a P=P double bond and a CH_2 group) as the most stable of the series [4]. The authors conclude that stable non-cyclic structures are the ones containing the maximum number of C-H bonds, while P-H bonds have the tendency to destabilize the molecules. The hybridization of the carbon atom also influences the models' stability: the presence of an sp^3 carbon atom leads to a more stable structure, while an sp^2 one has the opposite effect. However, this pattern does not apply in our case, most likely due to the presence of the oxygen atom.

Calculated P=C, P=P, P=O and P≡C distances are in the normal range for multiple-bonded phosphorus atoms. The P≡C bond lengths in **IV.3** and **IV.4** (1.554 and 1.547 Å) are slightly longer than that measured by X-ray for $\text{Mes}^*\text{C}\equiv\text{P}$ (1.516(13) Å [11]), but in agreement with values reported in the gas phase [12].

For the diphosphaallene $\text{HP}=\text{C}=\text{P}(\text{O})\text{H}$ **IV.5**, the calculated P-C-P angle (170.1°) and the P=C bond lengths (1.638 Å for the trivalent phosphorus atom and 1.621 Å for the pentavalent one) are in agreement with experimental data [12]. A comparison with the geometrical parameters of $\text{Mes}^*\text{P}=\text{C}=\text{P}(\text{O})\text{Mes}^*$ is not possible, since its X-ray structure has not been determined, but they are similar to those reported for other heteroallenes, for example $\text{Mes}^*\text{P}=\text{C}=\text{PMes}^*$ measured through X-ray diffraction (172.52°, 1.630 and 1.634 Å, see Table 2) [13]. In all heteroallenic structures, the $\text{E}=\text{C}=\text{E}'$ bond angle (E, E': Si, Ge, P, As) is never the ideal 180° but slightly more acute [2]. This is also obtained for the model compound **IV.5** (for which the value of the P-C-P angle is 170.1°), which would imply that the lack of linearity is not the effect of packing in the solid state, but a property inherent to the electronic structure of the diphosphaallene. To verify this further, we examined at the same level of theory model compounds including the allene

$\text{H}_2\text{C}=\text{C}=\text{CH}_2$ and its analogues obtained by replacing one or two terminal atoms with N or P. The geometry was linear, as expected, in the sole case of the allene. The replacement of only one terminal carbon atom with either N or P leads to a 5° deviation, while in the case of 1,3-diazaallene and 1,3-diphosphaallene $-\text{P}=\text{C}=\text{P}-$, the angle is around 170° . The NBO analysis shows in the case of the 1-aza- and 1-phosphaallenes ($-\text{E}=\text{C}=\text{C}<$, E = N, P) interactions between the lone pairs on the heteroatom and vacant antibonding orbitals (of both σ and π symmetry) localized on the $\text{C}=\text{C}$. In the case of the diphosphaallenes, charge transfers from a lone pair of one phosphorus atom to a σ antibonding orbital localized on the $\text{C}-\text{P}$ bond involving the other phosphorus are present, these interactions forcing the $\text{P}-\text{C}-\text{P}$ angle to narrow. This type of interaction is also present for the discussed derivative **IV.5** between the lone pair of the $\lambda^3\sigma^2$ P and an antibonding orbital of σ symmetry on $\lambda^5\sigma^3$ P-C; the orbitals involved are represented in Fig. 2.

<Figure 2>

<Table 2>

The data of Table 2 show that the $\text{P}-\text{C}-\text{P}$ angle is as expected highly dependent on the nature of the substituents on the phosphorus atom and of its hybridization [13-18]. A very strained angle of 115.05° has been reported for $i\text{-Pr}_2\text{NP}=\text{C}=\text{PPh}_2\text{Ni-Pr}_2$ [16], a derivative containing dicoordinated trivalent and tetracoordinated pentavalent phosphorus atoms in the PCP backbone. Thus, it can be seen that for $\lambda^5\sigma^3\text{-P}=\text{C}=\text{P-}\lambda^3\sigma^2$ and $\lambda^3\sigma^2\text{-P}=\text{C}=\text{P-}\lambda^3\sigma^2$ derivatives, the experimental data are in fair agreement with the structural parameters calculated herein.

The Mulliken charges calculated for **IV.5** are given in Fig. 3.

<Figure 3>

The difference between the calculated charges on the two phosphorus atoms are in agreement with the experimental data: the $\text{P}=\text{C}$ double bond containing the $\lambda^5\sigma^3$ phosphorus atom is computed to be more polarized than the one with the $\lambda^3\sigma^2$ phosphorus atom and is indeed more reactive towards even weakly acidic derivatives. This has been experimentally observed by the preferential addition of water to the $\lambda^5\sigma^3\text{P}=\text{C}$ double bond in $\text{Mes}^*\text{P}=\text{C}=\text{P}(\text{O})\text{Mes}^*$ [7].

The model compound $\text{Mes}^*\text{P}=\text{C}=\text{P}(\text{O})\text{Mes}^*$ has also been investigated at the B3LYP/6-311++G(d,p) level of the theory, and the geometry parameters are similar to those obtained for $\text{HP}=\text{C}=\text{P}(\text{O})\text{H}$: 1.635 Å for the P1-C bond, 1.620 Å for P2-C and 1.497 Å for the P-O distance, and also in agreement with the experimental values shown for the compounds in Table 2. The energy difference between $\text{Mes}^*\text{P}=\text{C}=\text{P}(\text{O})\text{Mes}^*$ and the Mes^* -substituted derivative **II.1** decreases to 23.11 kcal mol⁻¹ when compared to the hydrogen-substituted analogues (36.30 kcal mol⁻¹). This could be an argument in the favor of the stabilization offered by steric hindrance in such compounds, which was observed experimentally, since $\text{Mes}^*\text{P}=\text{C}=\text{P}(\text{O})\text{Mes}^*$ has been obtained and isolated.

Single point calculations have also been performed for all isomers by higher correlation methods CCSD(SDQ) and MP4 with the 6-311++G(d,p) basis set, in order to compare them with DFT calculations. The results maintain the relative energy ordering, with the exception of structures **IV**, for which **IV.3** is found to be the minimum of the series. The structure of interest **IV.5** is higher in energy than the **II.1** model compound by 39.08 kcal mol⁻¹ (CCSD/6-311++G(d,p)) and 37.90 kcal mol⁻¹ (MP4(SDQ)/6-311++G(d,p)), respectively. The calculated energies are given in Table 3.

<Table 3>

For the acyclic series, the Wiberg bond order [19] has also been calculated at the B3LYP/6-311++G(d,p) level, and a NBO [20] analysis was performed. The results are given in Table 4. For the model compound $\text{HP}=\text{C}=\text{P}(\text{O})\text{H}$ **IV.5**, the calculated bond orders are 1.89 for the $\lambda^3\sigma^2$ P-C bond and a lower order, of 1.57, for the $\lambda^5\sigma^3$ P-C one. As expected, for the triplet state **IV.7**, the bond orders are much smaller than for the singlet state **IV.6**.

<Table 4>

The lower bond order is explained by the NBO analysis which shows that second-order interactions occur between the lone pairs on the O atom and the antibonding orbitals of both σ (represented in Fig. 2) and π symmetry localized on $\lambda^5\sigma^3$ P-C bond (Fig. 4) leading to a population of the latter and thus the lowering of the bond order.

<Figure 4>

Summary

Although the phosphavinylidene(oxo)phosphorane $\text{HP}=\text{C}=\text{P}(\text{O})\text{H}$ is calculated to be one of the least stable isomers of the CH_2OP_2 formula (if we exclude carbenes and phosphinidenes), its corresponding bis(supermesityl) substituted derivative $\text{Mes}^*\text{P}=\text{C}=\text{P}(\text{O})\text{Mes}^*$ has been experimentally obtained, while the other possible isomers were not stabilized until now. It should be possible to obtain three-membered ring heterocycles with $\text{P}=\text{C}$ or $\text{P}=\text{P}$ double bonds and acyclic compounds with a $\text{P}=\text{C}-\text{P}$ or a $\text{P}\equiv\text{C}$ unit, which are calculated to be more stable, pending a judicious choice of substituents.

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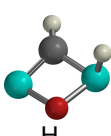
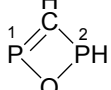
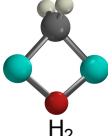
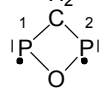
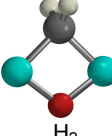
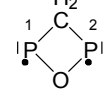
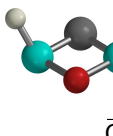
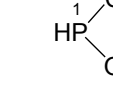
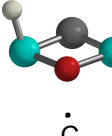
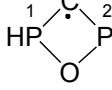
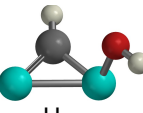
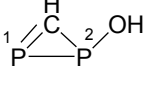

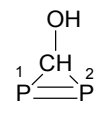
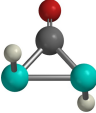

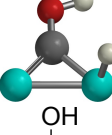
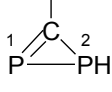
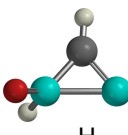
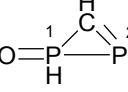
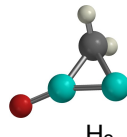
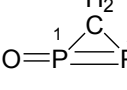
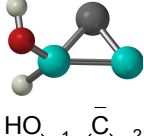
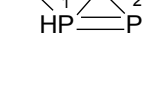
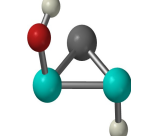
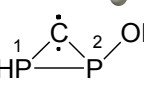
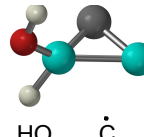
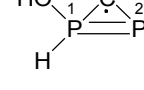
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Tables

Table 1 Selected bond lengths (Å) for CH₂OP₂ isomers

I	1	2	3	4	5
	 	 	 	 	 
	2 <i>H</i> -1,2,4-oxadiphosphete	oxadiphosphetane-2,4-diyl diradical, triplet	oxadiphosphetane-2,4-diyl diradical, singlet	1,2,4-oxadiphosphetan-3-ylidene, <i>trans</i> , singlet	1,2,4-oxadiphosphetan-3-ylidene, <i>trans</i> , triplet
P1-C	1.681	1.882	1.866	1.755	1.808
P1-O	1.699	1.710	1.679	1.723	1.728
P2-C	1.821	1.882	1.866	1.754	1.808
P2-O	1.725	1.710	1.679	1.723	1.728
II	1	2	3	4	5
	 	 	 	 	 
	hydroxydiphosphirane	diphosphiren-3-ol	diphosphiran-3-one <i>trans</i>	2 <i>H</i> -diphosphiren-3-ol	1 <i>H</i> -diphosphirene-1-oxide
P1-C	1.664	1.865	1.872	1.660	1.753
P2-C	1.784	1.865	1.872	1.828	1.691
P1-P2	2.243	2.044	2.323	2.313	2.181
P-O	1.698	-	-	-	1.493
C-O	-	1.404	1.187	1.332	-
II	6	7	8	9	
	 	 	 	 	
	2 <i>H</i> -diphosphirene-1-oxide	hydroxydiphosphiren-3-ylidene, singlet	hydroxydiphosphiran-3-ylidene, triplet	hydroxydiphosphiren-3-ylidene, triplet	
P1-C	1.765	1.800	1.745	1.656	
P2-C	2.060	1.725	1.771	1.803	
P1-P2	1.982	2.081	2.409	2.199	
P-O	1.486	1.638	1.659	1.635	
C-O	-	-	-	-	

III	1	2	3
	phosphinylidene-oxaphosphirane isomer Z	phosphinyl-oxaphosphirene	oxaphosphiran-3-yl-phosphinylidene singlet
P1-C	1.806	1.695	1.890
C-O	1.333	1.293	1.439
P1-O	1.789	2.052	1.708
P2-C	1.686	1.829	1.745

IV	1	2	3	4	5
	[oxo(Z)phosphinid enemethyl]phosphine	[oxo(E)phosphinid enemethyl]phosphine	hydroxy-phosphinylidynem ethyl)-phosphine	(phosphinylidynem ethyl)phosphine oxide	phosphavinylidene (oxo)phosphorane
P1-C	1.682	1.685	1.554	1.547	1.638
P2-C	1.828	1.829	1.778	1.781	1.621
P2-O	1.499	1.500	1.681	1.491	1.489

IV	6	7
	(phosphinylmethylidyne)phosphine oxide, singlet	phosphinylmethylidyne)phosphine oxide, triplet
P1-C	1.664	1.756
P2-C	1.657	1.767
P1-O	1.499	1.520

Table 2 Relevant geometrical parameters determined through X-ray diffraction on linear P-C-P systems

Compound	Ref.	Compound	Ref.
	13		14
	15		16
	17		18

Table 3 Relative energies (in kcal mol⁻¹, compared to **II.1**) obtained with high-correlated methods

Structure	R.E.(kcal/mol)	
	CCSD/ 6-311++G(d,p)	MP4(SDQ)/ 6-31++G(d,p)
I.1	3.70	3.28
I.2	18.04	18.71
I.3	23.16	21.88
I.4	70.84	71.36
I.5	78.15	85.16
II.1	0.00	0.00
II.2	8.22	8.40
II.3	12.69	18.51
II.4	16.16	16.25
II.5	17.15	16.06
II.6	22.11	20.47
II.7	52.07	52.36
II.8	67.61	70.52
II.9	85.60	87.48
III.1	30.08	29.15
III.2	44.89	43.73
III.3	63.46	63.55
IV.1	5.04	3.68
IV.2	6.84	5.53
IV.3	3.89	3.52
IV.4	10.77	9.45
IV.5	39.08	37.90
IV.6	56.36	55.53

Table 4 Wiberg bond orders for acyclic isomers of CH₂OP₂

IV	1	2	3	4	5	6	7
	$\text{HP}=\overset{1}{\underset{\text{H}}{\text{C}}}-\overset{2}{\text{P}}=\text{O}$	$\text{HP}=\overset{1}{\underset{\text{H}}{\text{C}}}-\overset{2}{\text{P}}=\text{O}$	$\text{P}\equiv\overset{1}{\text{C}}-\overset{2}{\underset{\text{H}}{\text{P}}}\text{OH}$	$\text{P}\equiv\overset{1}{\text{C}}-\overset{2}{\underset{\text{H}_2}{\text{P}}}\text{O}$	$\text{HP}=\overset{1}{\text{C}}=\overset{2}{\underset{\text{H}}{\text{P}}}\text{O}$	$\text{H}_2\overset{1}{\text{P}}-\overset{2}{\text{C}}-\overset{\text{O}}{\text{P}}$	$\text{H}_2\overset{1}{\text{P}}-\overset{2}{\underset{\cdot}{\text{C}}}-\overset{\text{O}}{\text{P}}$
P1-C	1.80	1.80	2.70	2.76	1.89	1.55	0.64
C-P2	0.94	0.96	1.02	0.89	1.57	1.68	0.59

Figure captions

Fig. 1 Relative B3LYP/6-311++G(d,p) energies (in kcal mol⁻¹) for the investigated CH₂OP₂ isomers

Fig. 2 NB orbitals involved in second order interactions contributing to the narrowing of the P-C-P angle in **IV.5**: (a) lone pair on P, (b) σ antibonding orbital on the P-C bond

Fig. 3 Mulliken charges calculated for isomer **IV.5**

Fig. 4 NB orbitals involved in second order interactions lowering the order of the $\lambda^5\sigma^3$ P-C bond: (a) lone pair on O, (b) π^* on the P-C bond