# Strong 1,4-P−O Intramolecular Interactions as a Source of Conformational Preferences in α-Stabilized Phosphorus Ylides

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For the first time, the existence of a strong intramolecular 1,4-interaction between the phosphorus atom and the oxygen atom in α-keto-stabilized ylides has been demonstrated by means of theoretical calculations. This interaction has a notable influence on the conformational preferences and rotational barriers of α-stabilized phosphorus ylides and bis-ylides.

## Introduction

The control of noncovalent interactions is currently one of the major challenges in synthetic procedures.[1] They can be used to assemble supramolecular species, and they can also govern conformational preferences.[2] An increasing number of such interactions is being reported. The existence of intermolecular C−H···C interactions involving phosphorus ylides has been recently proved.[3] Due to our current interest in the chemistry of α-stabilized P-ylides $Ph_3P{=}C(H)C(O)R$ (R = Me, Ph, OMe, $NMe_2$), we have studied these types of ligands in detail, and we have noticed the high tendency of the phosphonium P atom to be located near (mainly in cisoid form) to the carbonyl oxygen.[4] A Cambridge Structural Database search[5] reveals clearly the almost systematic preference of the phosphorus atom to be located cis with respect to the carbonyl oxygen. From a set of 79 observations of the unit P═C−C═O in different stabilized ylides, the main body of data shows cisoid conformations, with P−O distances in the range 2.67−3.32 Å, shorter than the sum of the van der Waals radii (3.35 Å) and with torsional angles P−C−C−O ($\theta$) near 0°. The remaining observations show P−O distances around 4 Å and $\theta$ around 180°, this last set of data corresponding mainly to ylides stabilized by an ester group: that is, with two oxygen atoms. The strong preference for the cisoid arrangement in the solid state thus seems to be clear. A recent, and very detailed, work in this area[6] allows us to obtain the same conclusion: that is, that the cisoid conformation (syn) is the only observed structure when a carbonyl group (ketone or aldehyde) is stabilizing an ylide function and that in the case of ester-stabilized ylides the two conformations are possible.

The structural conformation in solution of the ylides has also been studied,[7,8] and also two kinds of behavior arise. First, there are ylides which display the two possible rotational isomers, cisoid and transoid (e.g., $Ph_3P{=}C(H)CO_2Me$), and for which the energy of the rotational barrier around the $C_\alpha{-}C$ bond has been estimated[8d,f] (around 75 kJ mol$^{-1}$). Second, there are ylides which display a single isomer, which is reported to be cisoid (e.g., $Ph_3P{=}C(H)C(O)Me$), and for which it has not been possible to estimate the energy of the rotational barriers.[8e,g] Due to our interest in the conformational preferences of these ligands,[4] we have performed a theoretical DFT study (at the B3LYP level)[9] of different types of semistabilized and α-stabilized ylides and one α-stabilized bis-ylide, and in the present contribution we report the results of this study. Previous theoretical studies of phosphonium ylides have been employed

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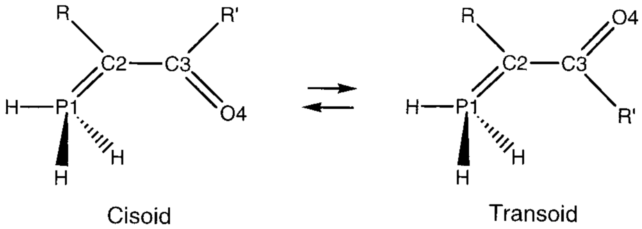

**Figure 1.**

**Table 1.** Calculated $\Delta E_1$ ($E_{trans}-E_{cis}$) and $\Delta E_2$ ($E_{TS}-E_{cis}$) Values (kJ mol$^{-1}$) for Ylides **1**−**6**

| | | $\Delta \boldsymbol{E}_1$ | $\Delta \boldsymbol{E}_2$ |
|---|---|---|---|
| $H_3P{=}C(H)C({=}CH_2)Me$ | **1** | 4.0 | 34.4 |
| $H_3P{=}C(H)C(O)Me$ | **2** | 43.3 (47.5)[a] | 112.6 (109.0)[a] |
| $H_3P{=}C(H)C(O)OMe$ | **3** | 8.2 | 84.9 |
| $H_3P{=}C(H)C(O)F$ | **4** | 1.5 | 90.5 |
| $H_3P{=}C(H)C(O)NH_2$ | **5** | 35.0 | 82.7 |
| $H_3P{=}C(Me)C(O)Me$ | **6** | 42.7 | 118.4 |

[a] CCSD(T)//B3LYP value.

to support the concept that the dominant resonance structure is the ylide form.[10]

## Results and Discussion

**1. DFT (B3LYP) Studies on Simple Ylides.** We have performed a theoretical DFT study (at the B3LYP level; basis set 6-31G (H atoms) and 6-31G(d) for the rest)[9] of some α-stabilized ylides of stoichiometry $H_3P{=}C(R)C(O)R'$ (R = H, R′ = Me (**2**), OMe (**3**), F (**4**), $NH_2$ (**5**); R = R′ = Me (**6**); see Figure 1). In this study, we have examined the conformational preferences and rotational barriers around the C2−C3 bond. Potential energy profiles for the rotational process were built. In all cases, the minima and transition state ($E_{TS}$) were characterized by analytically computing of the Hessian matrix. The energy difference between the transoid and cisoid conformations ($\Delta E_1 = E_{trans} - E_{cis}$) and the rotational barriers ($\Delta E_2 = E_{TS} - E_{cis}$) are collected in Table 1.

We have also studied the semistabilized ylide $H_3P{=}C(H)C({=}CH_2)CH_3$ (**1**), to evaluate the differences with its keto-stabilized homologue **2**. For ylide **1**, the cisoid conformation **1cis** is only slightly favored ($\Delta E_1$ = 4.0 kJ mol$^{-1}$). The value of $\Delta E_2$ (34.4 kJ mol$^{-1}$) matches very well with that determined by NMR methods for the related semistabilized ylide $Ph_3P{=}C(H)Ph$ (35.5 kJ mol$^{-1}$).[8i] This energy barrier can be mainly attributed to the loss of stabilization by resonance in the transition state.[11]

The ylide $H_3P{=}C(H)C(O)Me$ (**2**) shows a $\Delta E_1$ value of 43.3 kJ mol$^{-1}$. This value could be the clue to the understanding of the presence of a single isomer, both in the solid state and in solution. Additional arguments in favor of the cisoid geometry as the unique conformation for **2** comes from the comparative analysis of the calculated IR frequencies and NMR chemical shifts and those obtained experimentally.[12] The carbonyl stretch $\nu$(CO) for **2** appears at 1539 cm$^{-1}$, while the calculated values for the **2cis**, **2TS**, and **2trans** structures are 1599, 1791, and 1738 cm$^{-1}$, respectively. The $^1$H NMR chemical shifts for **2** in $CDCl_3$ are 3.67 ppm (C*H*) and 2.07 ppm (C*H$_3$*). Theoretical values were calculated using the extended base 6-311++G-(2d,2d) for all atoms and gave, for the **2cis** structure, an excellent agreement: 3.37 ppm (C*H*) and 1.96 and 2.09 ppm (C*H$_3$*). However, the obtained values for the **2trans** structure were quite different: 2.32 ppm (C*H*) and 2.11, 2.09, and 1.95 ppm (C*H$_3$*). The number of resonances for the methyl group in each compound reflects the symmetry of each molecule. The ylide **2cis** presents a plane of symmetry (the molecular plane) and gives two resonances, but the ylide **2trans** does not show elements of symmetry and gives three different resonances.

Moreover, the **2cis** structure (see Figure 2) deserves some comment. As can be seen from Table 2, the C2−C3 bond distance is shorter than a normal $\sigma$(C(sp$^2$)−C(sp$^2$)) single bond (1.484 Å)[10,13] and the P1−C2 and C3−O4 bond distances are elongated with respect to their usual values (1.688(3) and 1.697(3) Å in $Ph_3P{=}CH_2$[14] and 1.210 Å in ketones,[10,13] respectively). The P1−C2−C3 bond angle is 104.3°, notably smaller than the 120° expected, and moreover, the P···O intramolecular distance is 2.436 Å, suggesting a strong interaction between the P and O atoms. To analyze the energetics of the interaction of P−ylide with its α-substituents, we make use of group-transfer reactions:

$$H_3P{=}C(H)C(O)Me\ (\mathbf{2}) + CH_3{-}C({=}CH_2)H \rightarrow H_3P{=}C(H)C({=}CH_2)Me\ (\mathbf{1}) + CH_3{-}C(O)H$$

This kind of scheme provides a measure of the magnitude of the interaction between the groups and has been successfully used in the study of the interactions of carbonyl groups with their substituents.[11] The energy change for the group-transfer reaction of transoid structures (**1trans** and **2trans**) is 53.9 kJ mol$^{-1}$, indicating a stronger stabilization of the ketonic ylide **2** with respect to **1**. For cisoid structures (**1cis** and **2cis**) the energy change is still larger (93.3 kJ mol$^{-1}$) than for transoid. It is obvious that the increase of the energy change for cisoid structures must involve the formed P−O interaction. Thus, the energy difference between the two group-transfer reactions, 39.4 kJ mol$^{-1}$, corresponds to the P−O interaction energy, which is the main factor responsible for the stabilization of the cisoid conformation respect to the transoid one (43.3 kJ mol$^{-1}$).

Several structural changes take place along the rotational process (**2cis** → **2TS** → **2trans**; see Figure 2). As the dihedral angle P1−C2−C3−O4 ($\theta$) increases, the P1−C2 and C3−O4 bond distances decrease and the bond distance C2−C3 increases until the TS is reached ($\theta$ = 104°). The TS is, thus, the less conjugated structure. The value of the rotational barrier ($\Delta E_2$ = 112.6 kJ mol$^{-1}$) agrees with the experimental conclusion that this activation energy should be higher than 73.6 kJ mol$^{-1}$, by comparison with other ylides.[7a,8f,h] After the TS, the opposite behavior is observed due to a new gain of resonance (P1−C2 and C3−O4 increase and C2−C3 decreases). The high value of $\Delta E_2$ in **2** also supports the presence of a strong attractive interaction between the P and O atoms. This intramolecular interaction can be related to that recently described between E and N in $R_3EONMe_2$ compounds (E = Si, Ge, Sn).[15] However, in our model ylides it is a 1,4-interaction, giving rise to a four-membered ring.

To check on the methodology employed, we have recalculated the potential energy profile **2cis** → **2trans** using the CCSD(T) method at the B3LYP-optimized geometries. The differences in $\Delta E_1$ and $\Delta E_2$ are less than 4 kJ mol$^{-1}$ (Table 1), and the shape of the curve is essentially the same.

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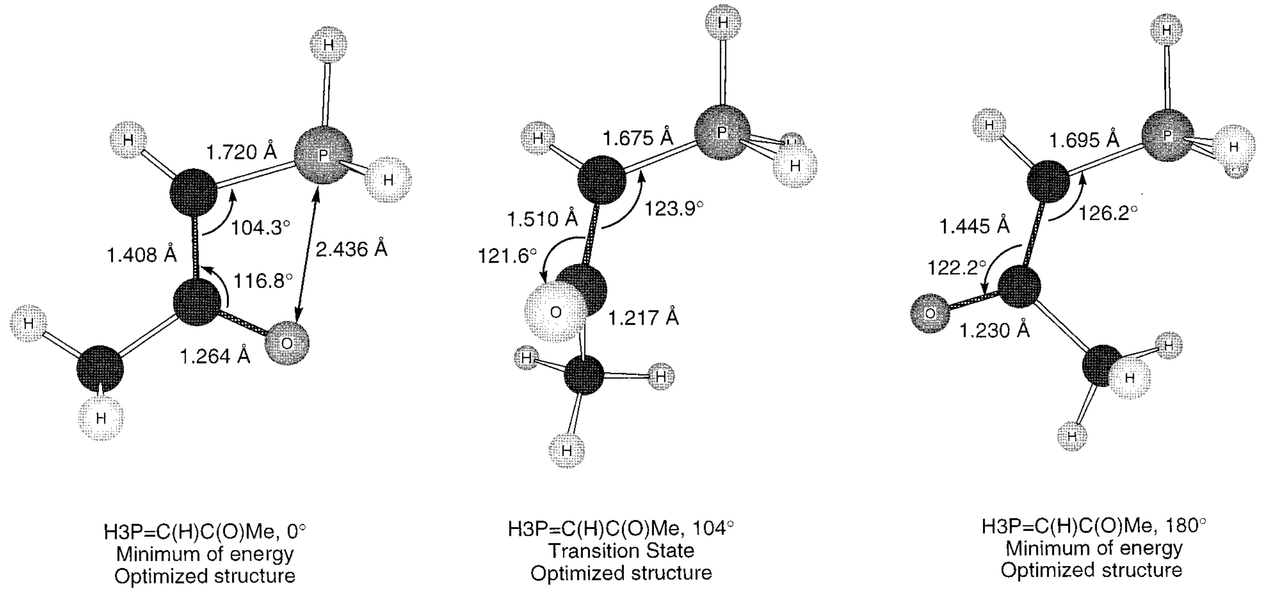


H3P=C(H)C(O)Me, 0°
Minimum of energy
Optimized structure

H3P=C(H)C(O)Me, 104°
Transition State
Optimized structure

H3P=C(H)C(O)Me, 180°
Minimum of energy
Optimized structure

**Figure 2.**

**Table 2.** Relevant Bond Distances (Å) and Angles (deg) and NPA Atomic Charges for Ylides **1**−**7**

| | *d*(12) | *d*(23) | *d*(34) | α(123) | *β*(234) | *θ*(1234) | *q*(P) | *q*(O) |
|---|---|---|---|---|---|---|---|---|
| **1cis** | 1.687 | 1.453 | 1.353[a] | 121.9 | 125.3[b] | −13.3 | +0.83 | −0.12[c] |
| **1TS** | 1.685 | 1.496 | 1.341[a] | 123.0 | 120.2[b] | 114.3 | +0.82 | +0.01[c] |
| **1trans** | 1.691 | 1.456 | 1.350[a] | 125.9 | 122.3[b] | −164.5 | +0.81 | −0.07[c] |
| **2cis** | 1.720 | 1.408 | 1.264 | 104.3 | 116.8 | 0.00 | +0.85 | −0.70 |
| **2TS** | 1.675 | 1.511 | 1.217 | 123.9 | 121.6 | 104.4 | +0.83 | −0.52 |
| **2trans** | 1.695 | 1.445 | 1.230 | 126.2 | 122.2 | −182.2 | +0.83 | −0.60 |
| **3cis** | 1.699 | 1.422 | 1.243 | 109.6 | 121.9 | 0.01 | +0.86 | −0.71 |
| **3TS** | 1.682 | 1.493 | 1.213 | 120.4 | 125.8 | 105.7 | +0.83 | −0.58 |
| **3trans** | 1.694 | 1.431 | 1.218 | 119.0 | 129.1 | 179.9 | +0.86 | −0.63 |
| **4cis** | 1.703 | 1.414 | 1.221 | 111.2 | 125.8 | 0.00 | +0.86 | −0.66 |
| **4TS** | 1.687 | 1.479 | 1.194 | 119.9 | 128.8 | 106.9 | +0.83 | −0.53 |
| **4trans** | 1.700 | 1.416 | 1.197 | 117.6 | 133.8 | 179.9 | +0.86 | −0.57 |
| **5cis** | 1.704 | 1.426 | 1.258 | 106.0 | 118.1 | 1.14 | +0.87 | −0.72 |
| **5TS** | 1.670 | 1.505 | 1.222 | 122.2 | 124.3 | 93.7 | +0.84 | −0.60 |
| **5trans** | 1.696 | 1.439 | 1.225 | 119.4 | 126.8 | −158.4 | +0.84 | −0.62 |
| **6cis** | 1.744 | 1.399 | 1.282 | 98.2 | 114.2 | -0.18 | +0.88 | −0.72 |
| **6TS** | 1.677 | 1.514 | 1.218 | 120.3 | 121.5 | 100.2 | +0.83 | −0.52 |
| **6trans** | 1.699 | 1.450 | 1.234 | 123.1 | 120.7 | −175.8 | +0.84 | −0.61 |
| **7cis-cis** | 1.705 | 1.419 | 1.299 | 106.8 | 115.3 | −0.01 | +0.86 | −0.78 |
| | 1.705 | 1.419 | | 106.8 | 115.3 | 0.00 | +0.86 | |
| **7cis-** | 1.715 | 1.424 | 1.283 | 100.9 | 112.2 | −0.78 | +0.88 | −0.72 |
| **trans** | 1.689 | 1.441 | | 122.9 | 120.8 | 184.1 | +0.84 | |
| **7trans-** | 1.701 | 1.469 | 1.232 | 117.9 | 123.1 | 136.7 | +0.83 | −0.61 |
| **trans** | 1.702 | 1.482 | | 118.1 | 122.6 | 128.4 | +0.83 | |

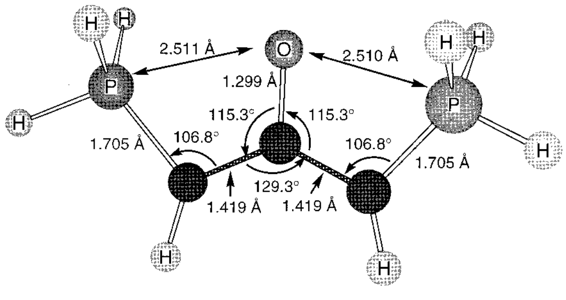
[a] *d*(C3C4). [b] *β*(C2C3C4). [c] *q*($CH_2$).

Results obtained with the methylated ylide **6** (see Tables 1 and 2) are very similar to that of **2**, showing that, in this case, the presence of a methyl group at $C_\alpha$ does not exert a significant influence over the rotational process. In contrast, the results for the ylide $H_3P{=}C(H)C(O)OMe$ (**3**) are quite different from those of **2** and **6**. The energy difference between cisoid and transoid conformations is small ($\Delta E_1 = 8.2$ kJ mol$^{-1}$), thus explaining the presence of the two rotational isomers in solution. This value is in good agreement with that calculated from NMR data for the ylide $Ph_3P{=}C(H)CO_2Me$ (3.89 ± 0.13 kJ mol$^{-1}$)[8d] and resembles the behavior of **1**. However, the rotational barrier of **3** is $\Delta E_2 = 84.9$ kJ mol$^{-1}$, higher than that found for **1** and close to the experimental value obtained from NMR data for $Ph_3P{=}C(H)CO_2Me$ (76.9 ± 2 kJ mol$^{-1}$).[8d]

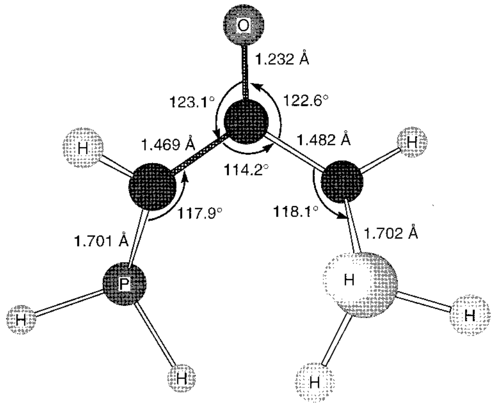
In ylide **3** the presence of one oxygen atom in both sides of the ylidic carbon C2 makes the P atom able to establish similar intramolecular interactions with the two oxygens, leading to a small energy difference between the two rotational isomers. The relatively high value of $\Delta E_2$ can be interpreted, as for **2**, not only as a consequence of the loss of resonance but also due to the loss of the intramolecular P···O interaction. Results obtained for the ylide $H_3P{=}C(H)C(O)F$ (**4**) are very similar to those of **3**: the two minima are isoenergetic ($\Delta E_1 = 1.5$ kJ mol$^{-1}$) and the value of $\Delta E_2$ is only slightly higher for **4** (90.5 kJ mol$^{-1}$) than for **3** (84.9 kJ mol$^{-1}$). These results suggest that the values of $\Delta E_1$ are strongly dependent on the nature of the carbonyl substituent. In the presence of a very electronegative substituent (F, O), the two conformations become almost isoenergetic, regardless of the electron-withdrawing (F) or electron-releasing (OMe) nature of the whole substituent. However, when weakly electronegative substituents are attached to the carbonyl (Me), the energy difference between the two conformers is important. The presence of only one electronegative atom seems to be crucial to discriminate between the two conformations. This set of observations could also point to an electrostatic nature of the strong P···O intramolecular interaction. Atomic charges on P and O atoms are consistent with this picture (Table 2). The introduction of an electron-releasing group such as $NH_2$ as the carbonyl substituent in $H_3P{=}C(H)C(O)NH_2$ (**5**) gives the expected results: the cisoid and transoid conformations are quite different in energy ($\Delta E_1 = 35.0$ kJ mol$^{-1}$).

The dependence of $\Delta E_2$ on the substituents is not so clear as that determined for $\Delta E_1$, probably due to the fact that this term should comprise, at least, three different parameters: the partial loss of resonance, the loss of the P···O interaction, and the hindered rotation around the C−C bond.[11] However, when the rotational process implies the rupture of the 1,4-P···O attractive interaction, the energy barrier is considerably higher (compare ylides **1** and **2**).

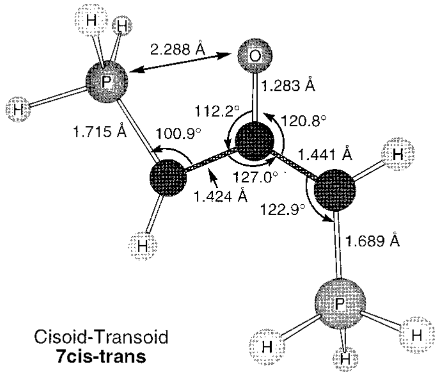
**2. Bis-Ylides.** Given the above results, it is not very surprising to find that the bis-ylide $Ph_3P{=}C(H)C(O)C(H){=}PPh_3$ (**7**) also shows strong conformational preferences, in such a way that *both* P atoms are located cisoid to the carbonyl oxygen (see Figure 3). In this case, we have calculated the energy value only for the extreme conformations cisoid-cisoid (**7cis-cis**), cisoid-transoid (**7cis−trans**), and transoid-transoid (**7trans-trans**). All of them are characterized as minima by analytically computing the Hessian matrix. As expected, the cisoid-cisoid conformation (**7cis-cis**) shows a lower value of the energy than



Cisoid-Cisoid
**7cis-cis**



Transoid-Transoid
**7trans-trans**



Cisoid-Transoid
**7cis-trans**

**Figure 3.**

the other two conformations. The energy differences are $\Delta E$(**7cis-trans**−**7cis-cis**) = 34.7 kJ mol$^{-1}$ and $\Delta E$(**7trans-trans**−**7cis-cis**) = 88.7 kJ mol$^{-1}$. It is noteworthy that the “first” change in energy due to the loss of one P−O interaction (34.7 kJ mol$^{-1}$) is smaller than that reported for **2** (43.6 kJ mol$^{-1}$), probably due to the fact that there is still a remaining P−O contact. Moreover, the “second” change in energy (88.7−34.7 = 54 kJ mol$^{-1}$) is notably higher than the first one, and the global change in energy (88.7 kJ mol$^{-1}$) is almost twice that reported for **2**. It is also worthy of note that the X-ray crystal structure of the bis-phosphonium derivative $[Ph_3PCH_2C(O)CH_2PPh_3](CF_3SO_3)_2$ (the protonated form of **7**) shows the cisoid-cisoid conformation.[16]

Important structural changes in the transition **7cis-cis** → **7cis−trans** → **7trans-trans** can be observed (see Figure 3 and Table 2). The **7cis-cis** structure shows a high degree of symmetry with respect to the C3−O4 axis, and its structural parameters are closely related to those of **2**. The most remarkable facts for the **7cis-trans** structure are the P1−O4 distance (2.288 Å), which is shorter than that obtained for **7cis-cis** (and even for **2**), and the notable difference between the halves of the molecule, with respect to the C3−O4 axis: (i) the P−C bond distances are quite different (P1−C2 = 1.715 Å; P6−C5 = 1.689 Å) as well as the C−C bond distances (C2−C3 = 1.424 Å; C3−C5, 1.441 Å), reflecting the different degree of delocalization, (ii) the bond angles of the skeletons P1−C2−C3−O4 and O4−C3−C5−P6 are also quite different (P1−C2−C3 = 100.9° vs P6−C5−C3 = 122.9° and C2−C3−O4 = 112.2° vs C5−C3−O4 = 120.8°), as a consequence of the P1−O4 interaction, and (iii) the loss of planarity of the O4−C3−C5−P6 fragment (dihedral angles O4−C3−C5−P6 = 184.13° and C2−C3−C5−P6 = 5.76°). In the case of the **7trans-trans** structure, the most remarkable fact is the complete loss of planarity in the energy minimum, the PCCO dihedral angles being 136.7° (P1−C2−C3−O4) and 128.43° (P6−C5−C3−O4). These facts also reflect the existence of strong conformational preferences in stabilized bis-ylide compounds, in which only one carbonyl oxygen can interact with two phosphorus atoms.

In addition, the different conformational isomers of bis-ylide **7** have been investigated by means of Bader analysis of electron density. Bader’s atoms in molecules (AIM) theory provides a set of practical tools for the study of bonding properties.[17] For the structure **7cis-trans**, the existence of an intramolecular P−O interaction was confirmed by the topological analysis of the electron density. This interaction was characterized by a bond critical point (bcp) in the electronic charge density ($\rho(r)$). Also, a ring critical point (rcp) was localized between the atoms P1, C2, C3, and O4, further proving the existence of the P−O interaction. Moreover, the value of the Laplacian of the charge density ($\nabla^2\rho(r)$) at the bcp (0.087 au) is low and positive. Thus, according to the theory of atoms in molecules, the positive value of the Laplacian at the bcp indicates a closed-shell interaction of electrostatic nature. In fact, a similar topological scheme was previously reported for a related intramolecular interaction between ketonic oxygen and nickel.[18] The map of the Laplacian of $\rho(r)$ computed for the structure **7cis-trans** is displayed in Figure 4A. From the Laplacian map we can observe two maxima of charge concentration (indicated by arrows), corresponding to the oxygen lone pairs. One of them points toward the charge-depleted valence shell of the phosphorus atom (P1), which is polarized toward the oxygen and shows an incipient charge transfer. This scheme also indicates an electrostatic interaction

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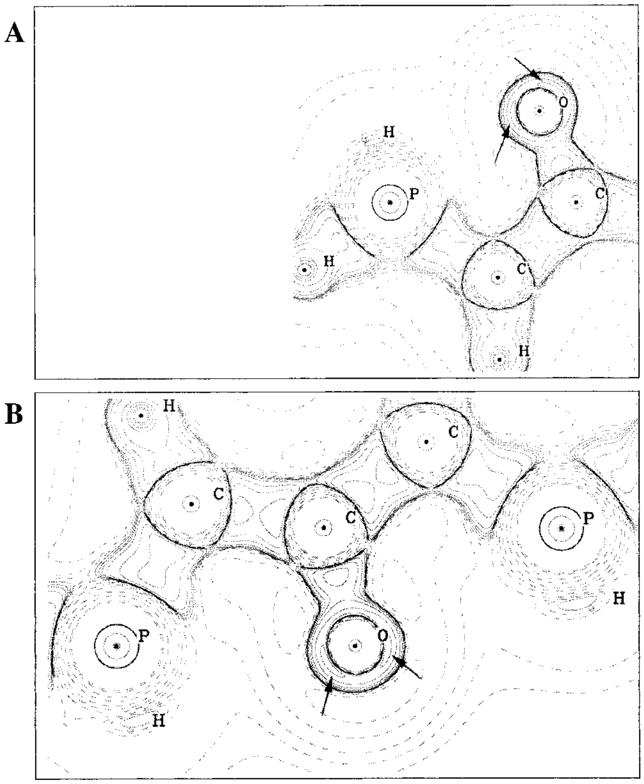

**Figure 4.** $\nabla^2\rho$(r) contour maps, in the plane containing the P−C−C−O skeleton, for the structures (A) **7cis-trans** and (B) **7cis-cis**. Negative contour maps of $\nabla^2\rho(r)$ are shown by dashed lines.

between the oxygen and the phosphorus. In the case of the structure **7cis-cis** it was not possible to localize any bcp between the oxygen and the phosphorus atoms. However, its Laplacian map (Figure 4B) depicts the same pattern as the structure **7cis-trans**, with each of the oxygen lone pairs facing one or the other phosphorus atom. This result, in conjunction with the arguments stated above, indicates that in the structure **7cis-cis** a P−O interaction also takes place, despite the fact that it is not being manifested by a bcp due to the longer P−O distance.

**Table 3.** Topological Properties at the Bond Critical Points and Distances in Å, of the Bis-Ylide Structures[a]

| | | **7cis-cis** | **7cis−trans** | **7trans-trans** |
|---|---|---|---|---|
| C2−C3 | $d$ | 1.419 | 1.424 | 1.469 |
| | $\rho(r)$ | 0.298 | 0.297 | 0.273 |
| | $\nabla^2\rho(r)$ | −0.784 | −0.762 | −0.669 |
| | $\epsilon$ | 0.252 | 0.263 | 0.184 |
| C3−C5 | $d$ | 1.419 | 1.441 | 1.482 |
| | $\rho(r)$ | 0.299 | 0.284 | 0.267 |
| | $\nabla^2\rho(r)$ | −0.784 | −0.725 | −0.640 |
| | $\epsilon$ | 0.252 | 0.204 | 0.162 |
| C3−O4 | $d$ | 1.299 | 1.283 | 1.232 |
| | $\rho(r)$ | 0.344 | 0.355 | 0.391 |
| | $\nabla^2\rho(r)$ | −0.338 | −0.256 | 0.176 |
| | $\epsilon$ | 0.011 | 0.006 | 0.061 |
| P1−C2 | $d$ | 1.705 | 1.715 | 1.701 |
| | $\rho(r)$ | 0.189 | 0.187 | 0.189 |
| | $\nabla^2\rho(r)$ | 0.076 | 0.074 | 0.073 |
| | $\epsilon$ | 0.355 | 0.325 | 0.377 |
| P6−C5 | $d$ | 1.705 | 1.689 | 1.702 |
| | $\rho(r)$ | 0.189 | 0.191 | 0.188 |
| | $\nabla^2\rho(r)$ | 0.076 | 0.113 | 0.066 |
| | $\epsilon$ | 0.355 | 0.398 | 0.372 |

[a] Distances ($d$) are given in Å. The electron charge density ($\rho(r)$), Laplacian ($\nabla^2\rho(r)$), and ellipticity ($\epsilon$) are given in atomic units.

In Table 3 are summarized the results of topological analysis of electron density for the P−C−C−O skeleton. The values of $\rho(r)$, $\nabla^2\rho(r)$, and ellipticity ($\epsilon$) at the bcp's were used to gauge the variation in charge density and bonding nature which occur upon structural changes. For all the C−C bonds the values of the Laplacian (large and negative) are indicative of shared interactions, characterized by a large accumulation of charge between the nuclei. The values of ellipticity, $\epsilon$, are relatively large, indicating a double-bond character; however, the values of $\epsilon$ decrease as the C−C bonds lengthen. Moreover, a correlation of bond length with bond strength is observed; thus, the longer the bond distance, the weaker the bond, which is manifested in lower values of $\rho(r)$. Therefore, the variations in topological properties as well as in distances reflect the different degrees of delocalization, which depend on whether the oxygen is interacting with phosphorus or not. For C−O bonds the values of $\epsilon$ are lower than those for C−C, showing that C−O bonds have less double-bond character. Recently, Molina and coworkers have analyzed the bonding nature of a phosphorus ylide ($H_3PCH_2$) using AIM theory.[19] The authors observed that large values of $\rho(r)$ and $\epsilon$ were compatible with a standard double bond ($H_3P{=}CH_2$), whereas the low values of $\nabla^2\rho(r)$ were not, concluding that the P−C bonds are covalent yet have significant polar interactions. In our case, where α-stabilized phosphorus ylides were considered, we observe similar trends. The values of $\rho(r)$ and $\epsilon$ are large and the values of $\nabla^2\rho(r)$ are low and positive, suggesting an interaction similar to that described by Molina and co-workers. Furthermore, the large and positive npa charges for P (see Table 2, range 0.83−0.88) and the large and negative npa charges for $C_\alpha$ (range −0.90 to −1.00) are compatible with an electrostatic interaction.

**3. Conclusion.** In conclusion, a strong P−O intramolecular attractive interaction is at work in α-stabilized phosphorus ylides and bis-ylides, governing their conformational preferences. Synthetic applications of this interaction are under investigation in our laboratories.

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