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# Molecular properties of the PCO radical: heat of formation and the isomerization pathways

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**Abstract** The potential energy surface of [P,C,O] system in the ground state was investigated by quantum chemical methods. Four different isomers were characterized at the B3LYP/aug-cc-pVTZ: COP (**i1**), cPCO (**i2**), PCO (**i3**), and CPO (**i4**). The linear species **i3** is the global minimum in the ground state surface, while **i4** is a bent structure, and **i2** is a cyclic isomer. In view to evaluate the bond nature of each isomer, a QTAIM and a NBO analyses were applied. The triangular species presents a ring critical point which confirms its cyclic structure instead of a T-shape one. The stability increases in the following order: **i3** > **i2** > **i1** > **i4**. The energy gap between **i3** and **i2** ranges from 49.20 to 51.15 kcal mol<sup>-1</sup>. The reaction barrier energies that converge into the direction of **i3** showed values around 10 kcal mol<sup>-1</sup>, while the reverse barriers are considerably large (62.85 kcal mol<sup>-1</sup>). The **i3** heat of formation at 298 K ranges from 11.83 to 19.41 kcal mol<sup>-1</sup>.

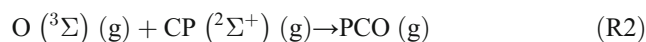
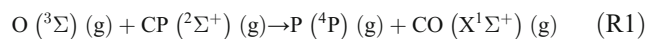
**Keywords** Charge analysis · PCO radical · Natural resonance theory · QTAIM · Renner-Teller · Resonance Weight

## Introduction

Phosphorous cosmic abundance is  $3 \times 10^{-7}$  relative to atomic hydrogen [1], and until now several phosphorous-bearing molecules have been detected in the interstellar medium:

PN [2–9], CP [4–6], HCP [9], C<sub>2</sub>P [10], and PO [11]. Phosphorous species have been identified in molecular clouds [2, 3], in carbon rich envelope of IRC +10216 [4–6, 9, 10], in the protoplanetary nebula CRL 2688 [5], in low-mass star forming region L1147 [8] and also in the supergiant star VY Canis Majoris [7, 11]. In Jupiter and Saturn atmospheres, the main atmospheric source of phosphorous bearing molecules is PH<sub>3</sub> [12–14]. Therefore, due to the high importance of phosphorous bearing molecules to planetary atmospheres and interstellar processes, the characterization of different phosphorus bearing species by experimental [15–17] and computational [18–20] studies have been performed along the years.

Millar [21] demonstrated by thermochemical models that the reactions between C<sub>n</sub>P species and the oxygen atom are one of the most important pathways to the destruction of organo-phosphorous species in dense interstellar clouds, like in Taurus molecular cloud (TMC-1). However, due to the low temperature in TMC-1, which is close to 10 K [21], the exchange reaction R1 may not be an important process. In general, exchange reactions are more important in environments with high temperatures, therefore the reaction between CP (<sup>2</sup>Σ<sup>+</sup>) and the oxygen could be a possible pathway to the formation of new phosphorous-oxygen bearing molecules like, for example, the PCO radical (process R2).



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In 1991, Mielke and Andrews [22] performed the first detection of PCO radical, nevertheless the author detected only the linear PCO (C<sub>∞v</sub>) isomer. Even though Li et al. [23] carried out an investigation of the PCO isomerization

process, the authors applied the CCSD(T)/6-311G(2df)/B3LYP/6-31G(d) method, which underestimated the barrier energies. In addition, Li et al. [23] restricted their investigation to the characterization of transition state structures and the geometry of the intermediates and did not take into account other molecular properties that can help in the understanding toward the molecular nature of each isomer, as well as the calculation of the heat of formation which are of great importance to comprehend the formation of the isomers in experimental conditions and interstellar environments and also to the development of more efficient models.

The purpose of this investigation is to perform an analysis of the PCO isomers in the ground state. The main reason why Mielke and Andrews [22] did not observe the formation of other isomers will be clarified here using quantum chemical calculations. In this study the following aspects will be evaluated: (i) the characterization of the PCO isomers stability; (ii) the geometrical parameters and an assessment of the spectroscopy properties; (iii) a charge analysis, as well as the bonding nature for each isomer; (iv) and a description of the barrier heights which link each species. The present study will employ the coupled cluster (CC) and the density functional theory (DFT) to describe the possible PCO isomers as well as the transition state structures that characterize the isomerization processes.

## Computational methodology

Stationary points on the potential energy surface of the reaction system were fully optimized, followed by evaluating harmonic vibration frequencies to characterize their nature as minima, or first-order saddle points. The geometry of the stationary points and the transition state structures were optimized at B3LYP exchange correlation functional [24, 25] with the aug-cc-pVTZ basis sets (aVTZ) [26, 27]. The transition states were confirmed by a subsequent frequency evaluation, and all connections between intermediates and transition states have been confirmed by intrinsic reaction coordinate (IRC) calculations [28, 29]. A tight convergence was employed in the optimization procedure and for the self-consistent field, while was also used the *ultrafine* grid.

Single point energies were also employed in the coupled cluster singles and doubles method with perturbative contribution of connected triples [30], CCSD(T). In order to confirm the efficiency of the CCSD(T) level to characterize the gap between each isomer, some multistep methods were also employed: W1BD [31], W1U [32], W1RO [33], G4 [34], G4MP2 [35], and CBS-QB3 [36].

A topological analysis with quantum theory of atoms in molecules (QTAIM) [37] and a natural bond orbital (NBO) analysis were performed to examine the bonding nature. The NBO algorithm [38] used was version 6.0, while the QTAIM

electron density analysis was carried out with the AIMALL program [39]. In the charge distribution different methods were employed: Mulliken population analysis, QTAIM [37], electrostatic potential (Chelp) [40], electrostatic potential using a Grid base method (ChelpG) [41], Merz-Singh-Kollman method (MK) [42, 43], and natural population analysis (NPA) [44]. The bond delocalization index (BDI) [45], Wiberg bond index ( $BO_{wi}$ ) [46], natural resonance theory bond index ( $BO_{nrt}$ ) [47–49], atom-atom overlap natural atomic orbital bond index ( $BO_{nao}$ ) [44], and the atom-atom overlap natural localized molecular orbitals/natural population analysis bond index ( $BO_{nlmo}$ ) [50] were applied in the bond order analysis. Charge distribution, bond order analysis, QTAIM and NBO investigation were obtained at the B3LYP/aVTZ level of theory.

In order to examine the heat of formation, the methodology outlined by Curtis et al. [51] was employed, which combines the *ab initio* and experimental values. In the total atomization energy, the elements heats of formation at 0 K was employed [51]: P ( $\Delta H_f^{0K} = 75.42 \text{ kcal mol}^{-1}$ ), C ( $\Delta H_f^{0K} = 169.68 \text{ kcal mol}^{-1}$ ) and O ( $\Delta H_f^{0K} = 58.99 \text{ kcal mol}^{-1}$ ).

Another multistep method employed in the energy analysis is called MSGX throughout the text. The electronic energy was obtained as in Eq. 1:

$$E_b = E_{HF} + \Delta E^{corr} + \Delta E^{full} + \Delta E^{rel} + \Delta E^{T-Q} + \Delta E^{SO} \quad (1)$$

where  $E_{HF}$  is the Hartree-Fock basis set limit energy extrapolated from aug-cc-pVnZ ( $n=T, Q, 5$ ) energies using the three-point extrapolation formula of Peterson et al. [52]  $\{E_{(n)} = E_{CBS} + A \exp[-n-1] + B \exp[-n-1]^2\}$ .  $\Delta E^{corr}$  is the correlation energy calculated by the CCSD(T) method and extrapolated to the basis set limit with the aug-cc-pVnZ ( $n=T, Q$ ) energies employing the two-point extrapolation formula of Halkier et al. [53]  $[E_{(n)} = E_{CBS} + B n^{-3}]$ .  $\Delta E^{full}$  is defined as the energy difference between all electrons and the frozen-core approximation, which is calculated with the CCSD(T) method employing the aVTZ basis sets.  $\Delta E^{rel}$  is the scalar relativistic contribution to the total energy of the molecule and the respective constituent atoms, determined by the difference between cc-pVTZ-DK and cc-pVTZ basis sets at the CCSD(T) level, where in the case of the CCSD(T)/cc-pVTZ-DK level was employed the Douglas-Kroll-Hess second-order scalar relativistic calculation [54, 55].  $\Delta E^{T-Q}$  refers to a higher order correction obtained by the difference between the BD(TQ) and CCSD(T) methods with the aVTZ basis sets, where BD(TQ) is the Bruckner Doubles method with perturbational corrections for both triple and quadruple excitations [56].  $\Delta E^{SO}$  represents the spin-orbit correction. Carbon and oxygen spin-orbit corrections were obtained from the excitation energies of Moore [57], while in the case of phosphorus no spin-

orbit correction was needed. For MSGX method was employed the geometries and the zero-point vibrational energies (ZPVE) obtained from B3LYP/aVTZ. All the electronic structure calculations in this study were carried out with the GAUSSIAN 09 quantum chemistry code [58].

## Results and discussion

Four different stationary points can be produced from [P, C, O] potential energy surface. In Table 1 can be seen the calculated electronic properties of each isomer using the B3LYP/aVTZ method. The vibrational frequencies and their respective intensities are also presented in Table 1.

The first isomer presented in Table 1 is the **i1** species, which is produced from the interaction between a phosphorus atom and CO molecule. The P–O distance in **i1** is 0.408 Å higher than the experimental P–O bond length of phosphorus monoxide [59]. Comparing the P–O distance between **i1** and the NOP ( $C_s$ ,  $^1A'$ ) radical, one can see a high similarity with our results, where P–O bond length ranges from 1.7726 to 1.8097 Å with the CCSD(T)/a( $n+d$ )Z ( $n=D,T,Q$ ) [60] method. Nevertheless, lower values are also observed for P–O bond length when taking into account HPCO [61] and the [C, $n$ -H,P,O] structures [62]. In addition, it is noteworthy that when we considered the **i1** C–O bond length it is observed as a very similar value with the experimental C–O bond length of the carbon monoxide, 1.1283 Å [63].

Now we turn our attention to the second isomer, the **i2** radical, which is the only cyclic isomer detected in the ground state with  $C_s$  symmetry. In **i2**, its angle value determined is very similar to other cyclic triatomic radicals previously described in the literature, as CNS [64], BCP [65], and SiCN radical [66]. Nevertheless, lower angle values are also described for other cyclic molecules in the literature, as in the case of  $C_2P$  [67], NOP [60], and GeCN radical [68]. In contrast, when we compared with the analogous cyclic structure NCO, an angle value 15 % smaller than in **i2** [69] was observed.

Considering the four isomers described in this study, the linear species **i3** is the global minimum on the ground state

surface, and **i4** is a bent structure with a  $C_s$  symmetry. Moreover, the C–P bond length of **i3** and **i4** radicals are similar to the results determined for BCP radicals [65] and XCP structures ( $X = H, F, Cl$ ) [70], and smaller than those observed for PCN isomers [71].

Another important issue, which needs to be addressed here, is the C–O stretching mode. Mielke and Andrews [22] only detected the  $\nu(C-O)$  mode, observed at  $1912.7\text{ cm}^{-1}$ , which was attributed to **i3**. Observing the intensity of each vibrational frequency among the four isomers, it is noteworthy that the **i3**  $\nu(C-O)$  intensity is the highest one among the four isomers, and if compared with the available vibrational experimental data a difference of  $64.8\text{ cm}^{-1}$  is seen. In addition, in **i1** the  $\nu(C-O)$  mode presents a result close to the experimental value of the CO molecule ( $2169.81\text{ cm}^{-1}$ ) [63], which would suggest the absence or a very weak P–O bond.

Examining the **i3** isomer, we notice a Renner-Teller coupling. The Renner-Teller effect can be characterized by two constants: the Renner parameter ( $e$ ) and the average harmonic bending frequency ( $\omega$ ). The Renner parameter,  $e$ , is a dimensionless constant that explains the Renner-Teller splitting of a bending potential, and it is used to assess the magnitude of the vibronic interaction [72]. In the case of **i3**, the Renner parameter is  $-0.1288$  which is similar to the results calculated by Leonard et al. [73] for the analogous species NCO, and also with other triatomic species [74, 75]. The fact that the Renner parameter is negative indicates that the potential surface matching to the asymmetric bending motion, with respect to the molecule plane, lies above the symmetric bending motion. Conversely, the average **i3** harmonic bending frequency is  $412.80\text{ cm}^{-1}$ .

The dipole moment of each isomer is also presented in Table 1. Before proceeding with the discussion of the dipole moment, it is important to mention that the dipole moment value is a significant parameter to radio observations in the interstellar medium and to future detection of new species [1]. The highest dipole moment is seen for **i2**, which is almost two times higher than for the other species. Due to its high dipole moment value, **i2** isomer may become an important candidate to future microwave spectroscopic studies.

The calculated atomic charge value to each isomer is presented in Table 2. A very common feature with other studies

**Table 1** Bond lengths (Å), angles ( $^\circ$ ), dipole moments ( $\mu$ , Debye), rotational constants (MHz), vibrational frequencies ( $\text{cm}^{-1}$ ) and their respective intensities [ $\text{km mol}^{-1}$ ] for each species in the ground state obtained with the B3LYP/aVTZ method

| Isomer                                 | Geometry |       |       |       | $\mu$ | Rotational constant         | Vibrational frequency |                        |                        |                           |
|----------------------------------------|----------|-------|-------|-------|-------|-----------------------------|-----------------------|------------------------|------------------------|---------------------------|
|                                        | P–O      | P–C   | C–O   | aPCO  |       |                             | $\nu_1$               | $\nu_2$                | $\nu_3$                | $\nu_4$                   |
| <b>i1</b> ( $^2\Pi$ , $C_{\infty v}$ ) | 1.884    |       | 1.151 | 180.0 | 0.72  | 5479.97                     | 215.92 [ $\pi$ , 0]   | 236.73 [ $\sigma$ , 7] | 280.91 [ $\pi$ , 1]    | 1894.18 [ $\sigma$ , 50]  |
| <b>i2</b> ( $^2A''$ , $C_s$ )          | 1.834    | 1.903 | 1.253 | 73.4  | 1.33  | 46954.03/ 11122.77/ 8992.56 | 434.88 [ $a'$ , 10]   | 632.45 [ $a'$ , 42]    | 1429.60 [ $a'$ , 85]   |                           |
| <b>i3</b> ( $^2\Pi$ , $C_{\infty v}$ ) |          | 1.666 | 1.161 | 180.0 | 0.81  | 5679.92                     | 413.89 [ $\pi$ , 3]   | 471.11 [ $\pi$ , 0]    | 737.18 [ $\sigma$ , 1] | 1977.46 [ $\sigma$ , 606] |
| <b>i4</b> ( $^2A''$ , $C_s$ )          | 1.487    | 1.660 |       | 151.1 | 0.89  | 225969.05/ 7903.12/ 7636.06 | 172.78 [ $a'$ , 15]   | 895.44 [ $a'$ , 21]    | 1246.33 [ $a'$ , 44]   |                           |

**Table 2** Atomic charges for phosphorus (qP), carbon (qC), and oxygen atom (qO) with different methods

| Isomer    |    | QTAIM | NPA   | Mulliken | Chelp | ChelpG | MK    |
|-----------|----|-------|-------|----------|-------|--------|-------|
| <b>i1</b> | qP | 0.19  | 0.09  | 0.13     | 0.07  | 0.07   | -0.16 |
|           | qC | 1.10  | 0.53  | 0.07     | 0.03  | 0.03   | -0.07 |
|           | qO | -1.29 | -0.61 | -0.20    | -0.10 | -0.10  | 0.23  |
| <b>i2</b> | qP | 0.61  | 0.45  | 0.39     | 0.18  | 0.13   | 0.14  |
|           | qC | 0.59  | 0.15  | -0.14    | -0.15 | -0.13  | -0.14 |
|           | qO | -1.20 | -0.60 | -0.25    | -0.03 | -0.004 | 0.003 |
| <b>i3</b> | qP | 0.72  | 0.22  | 0.23     | 0.03  | 0.03   | -0.04 |
|           | qC | 0.36  | 0.19  | -0.05    | 0.12  | 0.12   | 0.22  |
|           | qO | -1.08 | -0.41 | -0.18    | -0.15 | -0.15  | -0.18 |
| <b>i4</b> | qP | 1.96  | 1.31  | 1.06     | 0.63  | 0.63   | 0.55  |
|           | qC | -0.67 | -0.45 | -0.44    | -0.29 | -0.29  | -0.24 |
|           | qO | -1.28 | -0.87 | -0.63    | -0.34 | -0.34  | -0.30 |

[76, 77] is the high magnitude of the values obtained with the QTAIM method when compared with other methodologies employed in this study. An advantage of the QTAIM method is that it is less dependent on the level of theory employed, and, in general, describes with a high accuracy the physical meaning of the analyzed chemical systems [37, 76, 77]. Regarding the mean absolute deviation (MAD) between QTAIM and the results obtained with the other methods, it can be seen that NPA shows the lowest MAD (0.64). The MK method presents the highest MAD value (0.84), while Chelp and ChelpG present almost identical values to each isomer, which is an indicative that the additional grid implemented in ChelpG did not show changes from Chelp values. It is noteworthy that MK, Chelp and ChelpG are atom-centered monopole models which display spherical symmetric atoms, whereas QTAIM is markedly anisotropic, i.e., QTAIM attributes an intramolecular view while MK, Chelp and ChelpG are

**Table 3** Bond order analysis with bond delocalization index (BDI), natural resonance theory bond index ( $BO_{nrt}$ ), Wiberg bond index ( $BO_{wi}$ ), atom-atom overlap natural atomic orbital bond index ( $BO_{nao}$ ), and atom-atom overlap natural localized molecular orbitals/natural population analysis bond index ( $BO_{nlmo}$ )

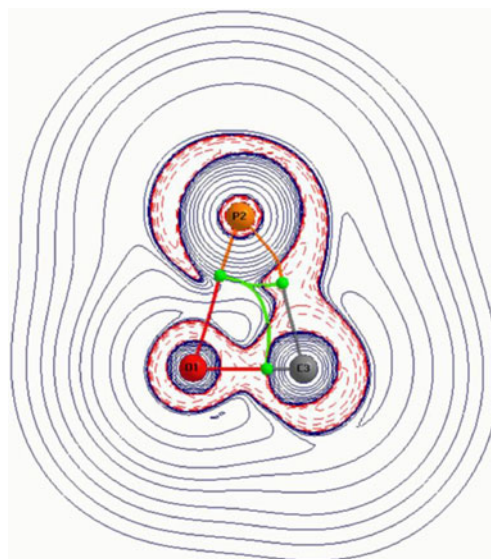
| Isomer    | Bond | BDI  | $BO_{nrt}$ | $BO_{wi}$ | $BO_{nao}$ | $BO_{nlmo}$ |
|-----------|------|------|------------|-----------|------------|-------------|
| <b>i1</b> | C–O  | 1.55 | 2.86       | 1.84      | 1.37       | 0.62        |
|           | P–O  | 0.79 | 1.02       | 0.42      | 0.46       | 0.11        |
| <b>i2</b> | P–C  | 0.99 | 0.98       | 1.09      | 0.64       | 0.24        |
|           | P–O  | 0.89 | 0.94       | 0.61      | 0.38       | 0.52        |
|           | C–O  | 1.35 | 2.02       | 1.48      | 1.17       | 0.46        |
| <b>i3</b> | P–C  | 1.74 | 1.98       | 1.71      | 1.34       | 0.87        |
|           | C–O  | 1.50 | 1.93       | 1.94      | 1.41       | 0.58        |
| <b>i4</b> | P–C  | 2.06 | 2.35       | 2.14      | 1.32       | 1.28        |
|           | P–O  | 1.17 | 2.38       | 1.39      | 0.80       | 0.38        |

**Table 4** Properties of bond critical points (BCPs), electronic charge density [ $\rho(r)$ ], Laplacian [ $\nabla^2\rho(r)$ ], local potential energy [ $V(r)$ ], local energy density [ $G(r)$ ], total energy density [ $H(r)$ ], ellipticity ( $\epsilon$ ), and ring critical point (RCP) for the different PCO isomers

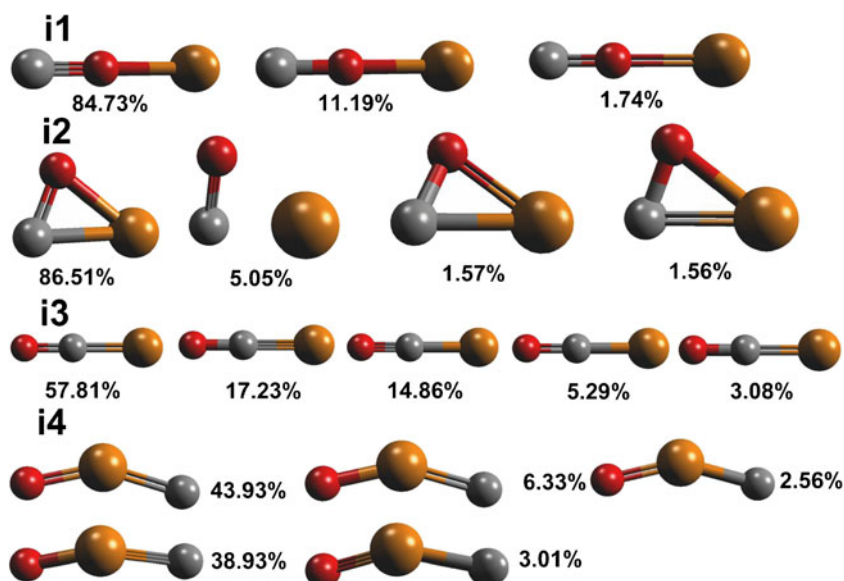
| Isomer    | Bond | $\rho(r)$ | $\nabla^2\rho(r)$ | $H(r)$  | $ V(r) /G(r)$ | $\epsilon$ |
|-----------|------|-----------|-------------------|---------|---------------|------------|
| <b>i1</b> | C–O  | 0.4495    | 0.6571            | -0.7915 | 1.8281        | 0.6571     |
|           | P–O  | 0.0803    | 0.2145            | -0.0433 | 1.4469        | 1.9825     |
| <b>i2</b> | P–C  | 0.1290    | -0.1398           | -0.0846 | 2.7048        | 0.1555     |
|           | P–O  | 0.1095    | 0.2524            | -0.0777 | 1.5517        | 4.1222     |
|           | C–O  | 0.3700    | -0.1791           | -0.6240 | 2.0773        | 0.2398     |
|           | RCP  | 0.1093    | 0.2724            | -0.0769 | 1.5302        |            |
| <b>i3</b> | P–C  | 0.1679    | 0.5367            | -0.1383 | 1.5075        | 0.5118     |
|           | C–O  | 0.4632    | 0.2050            | -0.8437 | 1.9427        | 0.0043     |
| <b>i4</b> | P–C  | 0.1769    | 0.1079            | -0.1696 | 1.8628        | 1.0108     |
|           | P–O  | 0.2282    | 1.3541            | -0.1892 | 1.3586        | 0.0073     |

electrostatic potential-derived charge providing an external view of the charge density distribution [76–78].

In the **i1** isomer, the high charge modulus is more concentrated in the oxygen than in the carbon atom ( $|qO| > |qC|$ ) when we compare QTAIM and NPA methods. In the case of Mulliken, Chelp and ChelpG the highest positive charge is located on the phosphorus atom rather than in the carbon atom. Still examining the **i1** species, a particular situation is the MK method, which shows a contrary behavior when compared with other methods. In order to check out the accuracy of the charge methods, the second order perturbation energy ( $E_2$ ) which determines the strength between a donor and an acceptor NBO was calculated. For the **i1**  $E_2$  energy, the donation from the oxygen lone pair electrons [ $n_p(O)$ ] to the

**Fig. 1** Contour maps of the Laplacian distribution of the electronic charge density [ $\nabla^2\rho(r)$ ] for the **i2** isomer. Blue lines refer to  $\nabla^2\rho(r) > 0$ , while the red lines indicate  $\nabla^2\rho(r) < 0$ . The green lines represent the BCP path into the direction of RCP

**Fig. 2** NRT resonance weights for the PCO isomers. The resonance weights represent the mean values between  $\alpha$  and  $\beta$  orbitals



phosphorus antibond lone pair electrons [ $n_p^*(P)$ ] represent almost 45 % of the total energy necessary to stabilize this radical. Therefore, a negative charge to the oxygen atom would be expected, as it is found with all methods excepting the MK charge. Nevertheless, this low positive value observed of phosphorus charge is linked with the  $n_p(P) \rightarrow \pi_{CO}^*$  donation, which characterizes 14 % of the total stabilization energy.

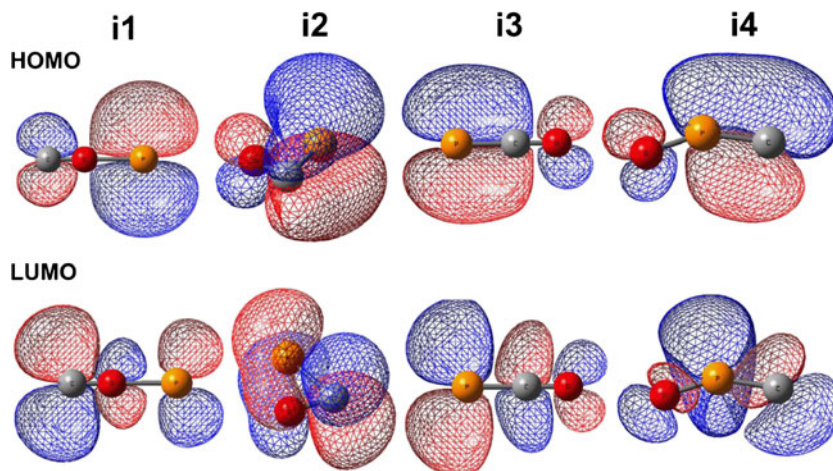
Analyzing the **i3** atomic charges, we can see that the QTAIM and NPA methods predict  $|qO| > |qP|$ , while the Mulliken charge shows an inverse behavior ( $|qO| < |qP|$ ), and Chelp and ChelpG predict  $|qO| \cong |qP|$ . Here one should pay attention to the fact that MK was the unique method which shows a negative charge on the carbon atom. Nevertheless, considering that  $n_p(O) \rightarrow \sigma_{PC}^*$  donation contributes with almost 65 % of the total energy to stabilize **i3**, a high negative charge on the oxygen atom would be expected, with NPA and QTAIM being the only methods displaying this behavior.

Based on the **i4** atomic charges, one can conclude **i4** is the only isomer for which all methodologies give the same mutual

relationship on the charge distributions, i.e.  $|qC| < |qO| < |qP|$ , with the phosphorous atom as the only one having a positive charge. The oxygen negative charge is attributed to the  $n_p(O) \rightarrow \pi_{PC}^*$  contribution amounting to the 31 % of the total stabilization energy. On the other side, the carbon negative charge comes from the  $n_p(C) \rightarrow \pi_{PO}^*$  and  $n_p(C) \rightarrow \pi_{PC}^*$  contribution which represent 7 % and 4 % of the isomer stability energy, respectively.

In **i2**, due to its cyclic geometry, is difficult to point out the highest contribution from the  $E_2$  analysis. For example, the highest contribution comes from  $\sigma_{PC} \rightarrow \sigma_{PO}^*$ ,  $\sigma_{PO} \rightarrow \sigma_{PC}^*$ , and  $n_p(P) \rightarrow \pi_{CO}^*$  donations which involve 18, 11 and 11 % of the radical stability, respectively. Nevertheless, there are also other minor contributions that also have an important role in this isomer stability, as the  $n_p(C) \rightarrow \sigma_{PO}^*$  donation and the donation from  $n_p(O)$  to the antibonding Rydberg orbitals of the carbon atom, where these interaction represent around 8 % of the total energy to stabilize this cyclic structure. Considering these interactions, we can see that NPA and QTAIM show the

**Fig. 3** HOMO and LUMO orbital plots (isovalue 0.05) for the PCO isomers at HF/aug-cc-pVTZ level



**Table 5** Relative energy gap (kcal mol<sup>-1</sup>) between each PCO isomer with the inclusion of ZPVE

| Method                          | i1    | i2    | i3   | i4    |
|---------------------------------|-------|-------|------|-------|
| CCSD(T)/6-311G(2d) <sup>1</sup> | 62.0  | 51.1  | 0.00 | 86.0  |
| W1BD                            | 68.44 | 49.66 | 0.00 | 80.60 |
| W1RO                            | 68.43 | 49.69 | 0.00 | 80.32 |
| W1U                             | 68.43 | 49.20 | 0.00 | 82.57 |
| G4                              | 68.76 | 51.15 | 0.00 | 82.64 |
| G4MP2                           | 68.99 | 50.60 | 0.00 | 81.28 |
| CBS-QB3                         | 69.77 | 51.12 | 0.00 | 79.45 |
| MSGX                            | 68.15 | 50.04 | 0.00 | 81.93 |

<sup>1</sup> Ref [23] with optimized structures at the B3LYP/6-311G(d) level of theory. <sup>2</sup> Optimization with B3LYP/aVTZ method

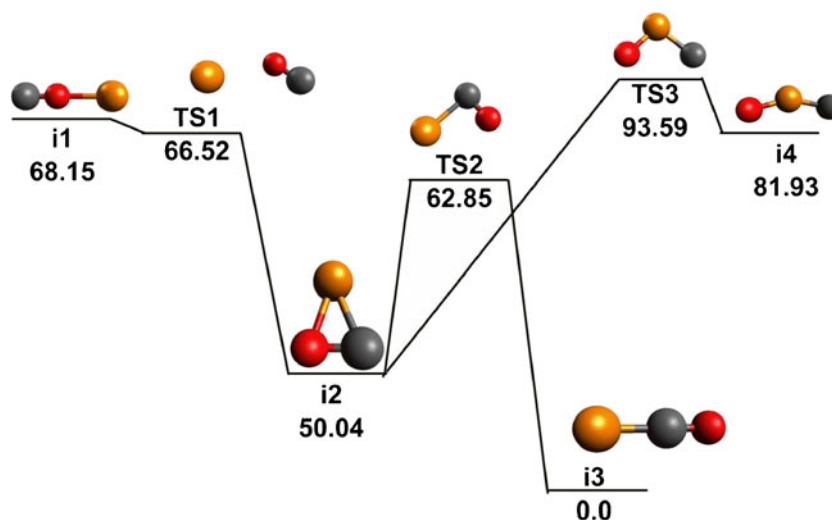
same behavior, where only the oxygen atom presents a negative charge. In contrast to this, Mulliken, Chelp and ChelpG show a negative charge on the carbon and oxygen atoms, while MK presents a negative charge only on the carbon atom.

Table 3 presents the bond order indexes from different methodologies. In **i1**, the C-O bond shows a value of 1.55 and 1.84 with BDI and BO<sub>wi</sub> indexes, respectively, which indicate a double bond nature. Nevertheless, in the case of BO<sub>nrt</sub> a value of 2.86 for the **i1** C-O bond was predicted, what is characteristic of a triple bond and was confirmed by a NBO analysis. Important properties can also be obtained by QTAIM analysis as shown in Table 4. In **i1**, with regard to the ellipticity ( $\epsilon$ ) of the P-O bond, we can notice a value three times higher than the same value found for the C-O bond, which emphasizes the instability of this bond. In fact, considering the H(r) negative sign of the P-O bond, we have a certain degree of covalence. In addition,  $|V(r)|/G(r)$  can also be an important tool to determine the covalent nature of the interactions. When  $|V(r)|/G(r)$  is greater than 2 we have an indication of covalent

interactions, lower than 1 for noncovalent interactions and ranging between 1 and 2 for partially covalent interactions [37]. In this case, **i1** P-O bond shows a  $|V(r)|/G(r)$  value of 1.44 which point out its partially covalent nature. In addition, by performing NRT analysis to characterize the electrovalency-covalency bond nature, we have detected a high ionic contribution in the **i1** P-O bond (83 %), and when performing a NBO analysis we found that this bond has a single bond character highly polarized toward the oxygen atom, with a BO<sub>nrt</sub> index of 1.02.

In the cyclic **i2** isomer, it was observed that the P-C and P-O bond orders are closer to 1 which indicate a  $\sigma$  bond. In **i2**, P-C bond is more polarized toward the phosphorus atom, while in the P-O bond it is more polarized toward the oxygen atom. On the other hand, the C-O bond shows a value higher than 1 with BDI, BO<sub>wi</sub>, BO<sub>nrt</sub> methods, which suggests a  $\pi$  nature which was confirmed by the NBO analysis. An inspection of the P-O bond shows that its moderate  $\rho(r)$  value and the positive value of  $\nabla^2\rho(r)$  are indicative of a closed-shell interaction. Considering the  $|V(r)|/G(r)$ , we can observe a value higher than 2 for the P-C and C-O bonds which confirm their covalent nature, while for the P-O bond it is 1.55 indicating a partially covalent character. It is important to realize that the high  $\epsilon$  value for the P-O bond also suggests a great instability. A further insight into **i2** QTAIM results show a ring critical point (RCP) which confirms that **i2** is a cyclic species. The RCP value is in good agreement with other studies [79, 80]. Figure 1 shows the representation of the Laplacian of electronic charge density as well as the BCPs path into RCP. It is important to notice that the absence of a RCP would be indicative of a T-shape structure, instead of a cyclic one. A straightforward inspection of T-shape and cyclic triatomic structures are discussed in Largo and collaborators [67, 79–83].

With regard to the **i3** and **i4** bonds, we can see a negative sign of H(r) and a  $|V(r)|/G(r)$  value between 1 and 2, which

**Fig. 4** Relative energy profile (in kcal mol<sup>-1</sup>) of the isomerization reactions between PCO isomers with the MSGX method including ZPVE

**Table 6** Heat of formation ( $\Delta_f H^\circ$ ) for each PCO isomer (kcal mol<sup>-1</sup>) at 0 K and 298 K

| Methods | i1                      |                           | i2                      |                           | i3                      |                           | i4                      |                           |
|---------|-------------------------|---------------------------|-------------------------|---------------------------|-------------------------|---------------------------|-------------------------|---------------------------|
|         | $\Delta_f H^\circ_{0K}$ | $\Delta_f H^\circ_{298K}$ | $\Delta_f H^\circ_{0K}$ | $\Delta_f H^\circ_{298K}$ | $\Delta_f H^\circ_{0K}$ | $\Delta_f H^\circ_{298K}$ | $\Delta_f H^\circ_{0K}$ | $\Delta_f H^\circ_{298K}$ |
| W1BD    | 87.94                   | 88.34                     | 69.16                   | 69.23                     | 19.50                   | 19.41                     | 100.11                  | 100.32                    |
| W1RO    | 87.63                   | 88.03                     | 68.89                   | 68.96                     | 19.20                   | 19.11                     | 99.52                   | 99.74                     |
| W1U     | 87.58                   | 87.99                     | 68.35                   | 68.42                     | 19.15                   | 19.06                     | 101.73                  | 101.94                    |
| G4      | 86.03                   | 86.41                     | 68.42                   | 68.49                     | 17.27                   | 17.17                     | 99.91                   | 100.16                    |
| G4MP2   | 85.79                   | 86.17                     | 67.40                   | 67.47                     | 16.80                   | 16.70                     | 98.08                   | 98.33                     |
| CBS-QB3 | 85.50                   | 86.14                     | 68.36                   | 68.46                     | 17.23                   | 17.15                     | 96.69                   | 96.91                     |
| MSGX    | 80.06                   | 80.47                     | 61.96                   | 62.03                     | 11.92                   | 11.83                     | 93.85                   | 94.07                     |

indicates their partially covalent nature. Nevertheless, the BDI,  $BO_{wi}$  and  $BO_{nrt}$  values of **i3** and **i4** bonds are closer to 2 indicating a  $\pi$  character.

In order to obtain the resonance structure weights, the natural resonance theory (NRT) was applied. Figure 2 shows the resonance weights in all four isomers. One notices that the high weights of **i1**, **i2** and **i3** resonance structures indicate very distinct values compared with the other two isomers, for which the secondary resonance structure shows a large separation with the respect to the starting reference structure at equilibrium. Li et al. [23] suggested that **i3** exhibits two main resonance structures; nevertheless the secondary structure demonstrates a negligible resonance weight. A particular case is **i4**, where the two resonance structures show very similar resonance weights, and by examining the  $BO_{nrt}$  we can see symmetric bond order indexes for P-C and P-O bonds.

Comparing the five bond order indexes applied in this study, we can observe that  $BO_{nlmo}$  presents more discrepant values than the other four methods. The main negative aspect related to the use of the  $BO_{nlmo}$  index is the difficulty to characterize the bond order and the  $\sigma/\pi$  nature because of their small values showing little variation among the different bonds. In this study, the  $BO_{nlmo}$  index showed values 60–80 % smaller than  $BO_{wi}$ , even though, in general, the  $BO_{nlmo}$  values are similar to the  $BO_{wi}$  ones [84]. Nevertheless, as demonstrated by Szarek et al. [84], in some cases  $BO_{nlmo}$  index leads to results that make the interpretation of the bond nature difficult, and this particularly occurs in the case of the elements belonging to the second and third period.

Figure 3 presents the frontier orbitals of the different PCO isomers; the highest occupied and the lowest unoccupied molecular orbitals HOMO and LUMO, respectively. In **i1**, the major contribution to HOMO is from  $n_p(P)$  followed by a small contribution from  $\pi^*_{CO}$ , while in LUMO we can see a  $\pi^*_{C-O}$  orbital character and a lower one from  $n_p^*(P)$ . In **i2**, the HOMO presents a substantial orbital character for  $n_p(P)$  and  $\sigma_{PC}$ , whereas LUMO presents a  $\sigma$  nondegenerate orbital between phosphorus and oxygen atoms. In the LUMOs of **i1** and **i2**, the most significant involvement is from  $\pi^*_{CO}$ , while  $n_p(P)$  presents a contribution almost 20 times lower. In **i3** and **i4**,

there is a high  $\pi_{PC}$  orbital character in both HOMOs. On the other hand, in **i3** a major  $n_p(P)$  and  $\pi^*_{CO}$  orbital character in the LUMO was observed, while in **i4** there is a high contribution from  $\pi^*_{PC}$  and  $\pi^*_{PO}$  orbitals.

The stability analysis is presented in Table 5. We can see that the energy gap between **i2** and **i3** ranges from 49.20 to 51.15 kcal mol<sup>-1</sup>, notwithstanding the gap between **i4** and **i3** is 79.45–83.12 kcal mol<sup>-1</sup>. In the case of **i2**, Li et al. [23] reported a similar value with the G4MP2 method, and the difference is around 1 kcal mol<sup>-1</sup> when compared with the MSGX method. Nevertheless, for **i4**, Li et al. overestimated the energy gap by almost 5 kcal mol<sup>-1</sup>, which reaches almost 7 kcal mol<sup>-1</sup> with the CBS-QB3 method. In this situation, considering these high energy gaps, only the global minimum isomer would be detected in a cold matrix trap, which may explain the results of Mielke and Andrews [22]. In **i1**, analyzing the basis set superposition error, a counterpoise correction [85] with CCSD(T)/aVQZ level presents an energy of 0.42 kcal mol<sup>-1</sup>. Nevertheless, it is important to comment that the counterpoise correction was not included in the results for this isomer.

Considering the barrier heights of the isomerization processes in Fig. 4, a feature which calls the attention is the negative barrier energy associated with the unimolecular rearrangement from **i1** to **i2**. This negative value occurs due to the weak nature of the P-O bond, where TS1 involves the displacement of the P atom from carbon monoxide leading to a flat potential energy surface. A similar situation was also found by Wang et al. [69], Bu [86] and Pan et al. [87]. In the

**Table 7** Adiabatic bond dissociation energies ( $D_e$ , kcal mol<sup>-1</sup>) of each PCO isomer with different methods at 0 K

|           | Bonds | W1BD   | W1RO   | W1U    | G4     | G4MP2  | CBS-QB3 |
|-----------|-------|--------|--------|--------|--------|--------|---------|
| <b>i2</b> | PC–O  | 111.64 | 111.49 | 110.56 | 111.58 | 112.01 | 108.81  |
|           | PO–C  | 94.33  | 94.17  | 94.68  | 91.68  | 90.93  | 92.84   |
| <b>i3</b> | P–CO  | 28.22  | 28.28  | 28.35  | 29.61  | 29.31  | 30.11   |
|           | PC–O  | 161.31 | 161.18 | 159.76 | 162.73 | 162.61 | 159.93  |
| <b>i4</b> | CP–O  | 80.70  | 80.86  | 77.18  | 80.09  | 81.32  | 80.48   |
|           | C–PO  | 63.38  | 63.54  | 61.30  | 60.19  | 60.25  | 64.51   |

case of the isomerization of CGeN to the cyclic isomer GeCN, Wand et al. [69] detected a barrier height of  $-1.40 \text{ kcal mol}^{-1}$  and  $-3.3 \text{ kcal mol}^{-1}$  for neutral and cationic species, respectively. Bu [86] characterizes a similar case for GaSO, however the author observed an inferior value from those showed in this study. In the case of the GeCP species, Pan et al. [87] observed a barrier height of  $-0.3 \text{ kcal mol}^{-1}$  for the isomerization of GePC to GeCP.

The transition state structure TS2 refers to the barrier energy associated with the unimolecular rearrangement from **i2** to **i3**. The separation energy between TS2 and **i2** is  $13 \text{ kcal mol}^{-1}$ , while Li et al. [22] predicted a barrier height of  $6.6 \text{ kcal mol}^{-1}$ , demonstrating the inefficiency of the CCSD(T)/6-311++G(2df) level to evaluate this isomerization reaction. Conversely, the cyclization reaction barrier of **i3** (**i3**→TS2→**i2**) is  $63 \text{ kcal mol}^{-1}$ . Examining the literature, it can be seen that this cyclization barrier energy is higher than the analogous processes in other triatomic radicals like CNS ( $46.2 \text{ kcal mol}^{-1}$ ) [66], GeCN ( $13.7 \text{ kcal mol}^{-1}$ ) [69], GeCP ( $22.7 \text{ kcal mol}^{-1}$ ) [87], and GeSiN ( $10.5 \text{ kcal mol}^{-1}$ ) [87].

The reaction barrier for the cyclization process starting in the bent isomer **i4** (**i4**→TS3→**i2**) is determined to be  $9.77 \text{ kcal mol}^{-1}$ . In addition, the reverse reaction (**i2**→TS3→**i4**) presents a reaction barrier four times higher than the cyclization one. Discussing these aspects, we can observe that the reaction barrier energies that converge into the direction of **i3** show values around  $10 \text{ kcal mol}^{-1}$ , while the reverse barriers are considerably higher, suggesting that the isomerization routes to the formation of **i3** are more favored energetically.

The heat of formation for each isomer at 0 K and 298 K is shown in Table 6. In **i3**,  $\Delta_f H^\circ_{298\text{K}}$  ranges from  $11.83$  to  $19.41 \text{ kcal mol}^{-1}$ , and for **i2**  $\Delta_f H^\circ_{298\text{K}}$  ranges from  $62.03$  to  $69.23 \text{ kcal mol}^{-1}$ . The highest values are observed with the W1BD and W1RO methods, while the lowest ones are seen with the MSGX method. On the other hand, G4 and G4MP2 demonstrated similar heat of formation values with W1BD, while CBS-QB3 shows comparable results with the G4 methodology.

The bond dissociation energy (BDE) for the PCO isomers are given in Table 7. Due to the weak strength of the P-O bond in **i1**, this isomer was not included in Table 7. In **i3**, C-O BDE is almost six times higher than the P-C one. Comparing the C-O BDE between **i2** and **i3**, we can see a decrease around  $50 \text{ kcal mol}^{-1}$ . In **i4**, a difference around  $20 \text{ kcal mol}^{-1}$  is seen between C-P and P-O BDEs. Here it is important to mention that these large dissociation energies of each species suggest that the generation and investigation of all these species are feasible in low-temperature. A particular case is the BDE of **i2** and the phosphorus product formation, which needs a spin-orbit investigation that will be performed in a future study involving the low-lying states of PCO isomers with the CASSCF/MRCI method.

## Conclusion

A quantum chemical study of PCO isomers was carried out. In this study, four different isomers were characterized. Among the isomers, the highest intensity for the **i3** C–O stretching mode may be the main reason for the detection of this species in experimental conditions. The analysis of the atomic charge distribution showed that Chelp and ChelpG present equal values to each isomer, which suggests that the additional grid implemented in ChelpG did not show high changes for Chelp values. The QTAIM presents the highest charge values, and its behavior was similar with the NPA method. A further insight on the **i2** QTAIM result shows a ring critical point (RCP), which confirms that **i2** is a cyclic species. Also, the highest dipole moment is seen for **i2**, which is almost two times higher than for the other species. This high **i2** dipole moment demonstrates that this species may be an important candidate to interstellar radio detections, or even to microwave spectroscopy studies. In addition, it can be noticed that the high weights of **i1**, **i2**, and **i3** resonance structures show that the secondary resonance structure indicates a large separation of the leading reference structure at equilibrium. Examining the relative energies, the most important aspect for the relative energies is the small reaction barrier energies that converge into the direction of the **i3** isomer. The reactions **i4** → **i2** and **i2** → **i3** showed barrier heights close to  $10 \text{ kcal mol}^{-1}$ , while the reaction **i1** → **i2** does not show a barrier energy, which implies an easier conversion to **i3** (contrary to the respective reverse reaction barriers that are very large). Heat of formation at 298 K for **i4** varies from  $94.07$  to  $101.94 \text{ kcal mol}^{-1}$ , and for **i2** ranges from  $62.03$  to  $69.23 \text{ kcal mol}^{-1}$ .

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