Theoretical study of the chemical reactivity of a class of trivalent phosphorus derivatives towards polyhaloalkanes: DFT study

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Abstract

In the current work, the chemical reactivity of some trivalent phosphorus derivatives $R_2PR'$ towards polyhaloalkanes $CCl_3POR'$ was studied by the quantum method DFT/B3LYP/6-311G(d,p). The introduction of substituents for the trivalent phosphorus derivative and polyhaloalkane allowed us to have more information on these reactions. On the one hand, the calculation of reactivity indices derived from the DFT/B3LYP/6-311G(d,p) method and the gap $\text{LUMO} - \text{HOMO}$ show that trivalent organophosphorus derivatives behave as nucleophiles, while polyhaloalkanes act as electrophiles. On the other hand, the calculation of the activation barrier and the determination of the free enthalpy variation prove that the kinetic and thermodynamic products of these reactions result from the nucleophilic attack of the phosphorus atom on the chlorine halogen. All these theoretical predictions are in very good agreement with the experimental results.

Keywords

Trivalent phosphorus derivatives · Polyhaloalkanes · DFT/B3LYP/6-311G(d,p) · Global indices · Transition state · Thermodynamic properties

Introduction

Most polyhalomethanes such as tetrachloromethane $CCl_4$ [1], chloroform $CHCl_3$ [2, 3], diethyl trichloromethyl phosphonate $CCl_3PO(OEt)_2$ [4, 5], and trichloromethylphosphine oxide $CCl_3PO(Ph)_2$ [6] react with trialkylphosphites through the participation of a single halogen atom. However, dichloromethyl ether [7] and N-(trichloromethyl)-dialkylamine [8] which are highly electrophilic polyhaloalkanes can substitute two or even three of their halogen atoms with dialkylphosphonyl groups. The introduction of an electron-withdrawing group strongly activates the halogen in position as in the case of trichloroacetonitrile ($CCl_3-CN$) which engages the three chlorine atoms by reacting with phosphites according to Fig. 1 [9].

Following this scheme, Sagina and Kukhar [9] expected trichloromethylphosphonate 2 to act in the same way as trichloroacetonitrile despite the low electron acceptor power of the dialkylphosphonyl group compared to the nitrile function.

The reaction carried out according to Fig. 1, at temperatures between 120 °C and 130 °C in the absence of solvent and catalyst, allowed the synthesis of bisphosphonate 3 with a yield of 82% from equivalent proportions of ($RO)_3P$ and $CCl_3PO(OR)_2$. The dichloromethylene bisphosphonate 3 thus obtained was only identified by infrared spectroscopy.

Furthermore, Sagina and Kukhar [10] have shown that bisphosphonate 3 is also obtained by reacting one mole of $CCl_4$ and two moles of phosphate ($RO)_3P$ according to Fig. 1. Phosphonate 2 is produced from phosphite ($RO)_3P$ and excess tetrachloromethane. The formation of dichloromethylene bisphosphonate via an SN2 nucleophilic attack on carbon excluding the possibility of a radical mechanism has been proposed [9].
Bakkas and collaborators [11–13] resumed the experimental study of reactions 1a and 2a since the presence of bisphosphonate 3 has never been proven before in the reaction of CCl₄ and (EtO)₃P. According to Fig. 1, they showed that (i) among other phosphorus compounds, the phosphonate EtCCl₂P(OEt)₂ is obtained rather than bisphosphonate 3, and (ii) bisphosphonate 3 or its derivatives are obtained by a radical mechanism when 1a and 2a react under UV light.

It was concluded that the thermal reaction of triethylphosphite 1a with diethyl trichloromethyl phosphonate 2a takes place according to a nucleophilic attack of 1a on one of the chlorine atoms of 2a. This has been verified at room temperature by reacting [9] the polyhaloalkane 2a with the more reactive phosphinite (Ph)₂POCH₃ than the phosphite (EtO)₃P.

In the current study, we will perform a theoretical study using the DFT/B3LYP/6-311G(d,p) method, of the reaction of CCl₃POR′′₂ with R₂PR’ in order to specify its reaction mechanism. This consists in checking Fig. 2 which supposes that the phosphorus atom, considered a nucleophilic center, will attack the carbon (A_C) or the chlorine (A_Cl) of the polyhaloalkane CCl₃POR′′₂ assumed to be electrophilic centers.

**Calculation details**

The quantum calculations were performed using Gaussian 09 [14]. The equilibrium geometries were visualized using the GaussView 5.0 program which can generate a three-dimensional arrangement serving as a starting point for geometry optimization at the quantum level. The geometry of neutral systems has been maintained for cationic and anionic systems used for local indices calculations. We used the density functional theory (DFT), an approach that is very widespread today. A double choice is necessary to perform the calculations: the type of functional and the atomic orbital base. The B3LYP/6-311G(d,p) [15, 16] level has been chosen here because of its satisfactory quality/cost ratio considering the size of our systems.

The localization of the transition states obtained by the B3LYP/6-311G(d,p) method was confirmed by the presence of one and only one imaginary frequency in the Hessian matrix. The IRC (intrinsic reaction coordinate) calculation [17] was performed to show whether the transition state is well related to the two minima (reagents and products). Furthermore, enthalpies, entropies, and free energies values were determined using standard statistical thermodynamics through calculation of the vibration frequencies [16].
Results and discussion

Study of structural and electronic properties

Geometrical parameters of reagents CCl$_3$PO(OEt)$_2$ and CCl$_3$PO(Ph)$_2$

Figure S1 presents the optimized geometries obtained by the B3LYP functional and the base 6-311G(d,p) and the numbering of the atoms of the most stable conformation of polyhaloalkanes CCl$_3$PO(OEt)$_2$ and CCl$_3$PO(Ph)$_2$.

The lengths, energies, and angles of the bonds involved in the studied reactions were determined from these optimized structures. There values are summarized in Table S1.

Results obtained show that the reactivity of the chlorine atoms of the two polyhaloalkanes [CCl$_3$PO(OEt)$_2$ and CCl$_3$PO(Ph)$_2$] does not have the same strength towards the most reactive site of the organophosphorus [P(OEt)$_3$ and (Ph)$_2$POCH$_3$].

Electronic properties: partial atomic charges

The use of Mulliken’s population analysis (MPA) [18] allows to determine Mulliken’s charges which help to estimate partial atomic charges using the DFT/B3LYP/6-311G(d,p) calculation method. Atomic charges were also determined using natural population analysis (NPA) [19] at the B3LYP/6-311G(d,p) level.

The results obtained for these electronic parameters are summarized in Table S2. Examination of the distribution of net charges at the most reactive sites of polyhalogénoalkanes [CCl$_3$PO(OEt)$_2$ and CCl$_3$PO(Ph)$_2$] allow us to state the following findings: (i) due to the negativity of its net charge, the carbon atom is an electron-rich site; (ii) since the chemical environment of the three chlorine atoms is different, then their positive charges are unevenly distributed and are, therefore, electron-deficient sites.

According to these results, we can consider carbon atom as a nucleophilic site whereas the chlorine halogen is more active towards a nucleophilic attack.

Table 1  Energies HOMO, LUMO, electronic chemical potential $\mu$, hardness $\eta$, electrophilicity $\omega$, and the overall nucleophilicity $N$ of the reagents: (EtO)$_3$P, (Ph)$_2$POCH$_3$, CCl$_3$PO(OEt)$_2$, and CCl$_3$PO(Ph)$_2$ (the values in eV)

| Reagents          | $E_{LUMO}$ | $E_{HOMO}$ | $\mu$  | $\eta$  | $\omega$ | $N$   | $\Delta\omega_1$ | $\Delta\omega_2$ |
|-------------------|------------|------------|--------|---------|----------|------|-------------------|-------------------|
| (EtO)$_3$P        | 0.689      | -6.940     | -3.125 | 7.629   | 0.640    | 2.428 |       |                   |
| (Ph)$_2$POCH$_3$  | -0.899     | -6.131     | -3.515 | 5.232   | 1.180    | 3.237 |       |                   |
| CCl$_3$PO(OEt)$_2$| -1.431     | -8.337     | -4.884 | 6.906   | 1.727    | 1.031 | 1.087             | 0.547             |
| CCl$_3$PO(Ph)$_2$ | -1.781     | -7.487     | -4.634 | 5.706   | 1.881    | 1.881 | 1.241             |                   |

\[ \Delta\omega_1 = \omega^{CCl_3PO(OEt)_2} - \omega^{(EtO)_3P} \]

Frontier orbital analysis

The concept of frontier molecular orbital (FMO) allows analyzing the reactivity of molecules in terms of interactions of the molecular orbitals of the reagents by considering only the most important interactions [20]. In the case of the reaction of trivalent phosphorus derivatives [P(OEt)$_3$ and (Ph)$_2$POCH$_3$] with polyhaloalkanes [CCl$_3$PO(OEt)$_2$] and CCl$_3$PO(Ph)$_2$, the charge transfer that takes place near the transition state mainly involves electrons from the nucleophile’s highest occupied molecular orbital (HOMO) to the electrophile’s lowest vacant molecular orbital (LUMO). As a result, the electron density associated with these electrons should explain the reactivity and selectivity of this reaction. The HOMO and LUMO can inform us about the mode of interaction between molecular entities.

Indeed, the HOMO acts as electron donor and the LUMO acts as electron acceptor. The calculation of the frontier orbital energy gap $\Delta\omega_{HOMO-LUMO}$ helps us to characterize the chemical reactivity and the kinetic stability of the molecule. It is known that a molecule with a small energy difference (gap) is polarizable and generally associated with high reactivity and low kinetic stability and is called a soft molecule [21].

From the values of the energies of the HOMO and LUMO molecular orbital boundaries determined by the DFT/B3LYP/6-311G(d,p) method, we have calculated the LUMO-HOMO energy difference for the two possible combinations of the studied system, the classification of the values of which is reported in Table S3 in decreasing order of magnitude.

As shown in Fig. S2, the orbital diagram gives a good qualitative indication of the reactivity of our system. It can be seen that the main interaction is between the LUMO of polyhaloalkanes [CCl$_3$PO(OEt)$_2$, CCl$_3$PO(Ph)$_2$] and the HOMO of organophosphorus compounds [P(OEt)$_3$ and (Ph)$_2$POCH$_3$].

Table S3 shows that the energy difference $E_{LUMO} - E_{HOMO}$ is smaller in the case of the reaction of diethyl trichloromethyl phosphonate CCl$_3$PO(OEt)$_2$ with diphenylmethyl phosphinite (Ph)$_2$POCH$_3$ than with triethylphosphite 1a. This explains the high reactivity of phosphinite (Ph)$_2$POCH$_3$ with phosphite.
(EtO)₃P with diethyl trichloromethyl phosphonate CCl₃PO(OEt)₂. We note that this reactivity increases with the substitution of the ethoxy group (−OEt) by a phenyl group (−Ph) which reduces the energy gap between the frontier orbitals.

The molecule CCl₃PO(Ph)₂ has the lowest energy gap between the LUMO and HOMO orbital (5.706 eV), justifying its high electro-acceptance power. Moreover, the (Ph)₂POCH₃ molecule has the smallest energy gap LUMO−HOMO (5.232 eV) compared to the (EtO)₃P molecule, confirming its higher electron-donor power with easy transfer of electrons from HOMO to the higher orbitals.

The latter is essentially the seat of nucleophilic attack of the phosphorus compounds P(OEt)₃ and (Ph)₂POCH₃. For the two modes of attack (Aₐ and Aₐ'), this analysis of the reaction correctly explains the regioselectivity observed experimentally [11–13] as well as the good concordance with the values of the free enthalpy variation ΔG₉.

Analysis of the overall properties of the reagents and prediction of the nature of the reaction mechanism

To clarify the character (electrophilic or nucleophilic) of the reagents studied, the DFT/B3LYP/6-311G(d,p) method was used to calculate the gap energies HOMO/LUMO for the two possible combinations; the results obtained are summarized in Table S4.

Results clearly show the gap energies corresponding to the HOMO combination of trivalent phosphorus derivatives [(EtO)₃P and (Ph)₂POCH₃]; the LUMO of the polyhaloalkanes [CCl₃PO(OEt)₂ and CCl₃PO(Ph)₂] is lower than that corresponding to the HOMO combination of [CCl₃PO(OEt)₂ and CCl₃PO(Ph)₂], and the LUMO of [(EtO)₃P and (Ph)₂POCH₃]. This proves that both trivalent phosphorus derivatives act as electron donors and polyhaloalkanes act as electron acceptors.

### Table 2

| Reagents       | Site K | Parr⁺(r) | Parr⁻(r) |
|----------------|--------|----------|----------|
| (EtO)₃P       |        |          |          |
| O₁            | 0.390  | 0.399    |          |
| O₂            | −0.014 | 0.026    |          |
| O₃            | −0.008 | 0.275    |          |
| O₄            | 0.007  | 0.222    |          |
| (Ph)₂POCH₃    |        |          |          |
| P             | 0.175  | 0.391    |          |
| O             | 0.005  | 0.111    |          |
| CCl₃PO(OEt)₂  |        |          |          |
| C₁            | 0.296  | 0.093    |          |
| C₂            | 0.260  | 0.118    |          |
| C₃            | 0.236  | 0.080    |          |
| C₄            | 0.197  | 0.200    |          |
| CCl₃PO(Ph)₂   |        |          |          |
| C₂₄           | 0.091  | −0.003   |          |
| C₂₅           | 0.096  | 0.017    |          |
| C₂₆           | 0.083  | 0.024    |          |
| C₂₇           | 0.050  | 0.021    |          |

### Table 3

| Systems              | Products          | ΔHₑ | ΔEₑ | ΔGₑ |
|----------------------|-------------------|-----|-----|-----|
| P(OEt)₃+CCl₃PO(OEt)₂ | P(CC₃1−2a)        | −24.606 | −25.400 | −21.283 |
|                      | P(CC₃1−2a)        | −44.501 | −45.637 | −42.630 |
| P(OEt)₃+CCl₃PO(Ph)₂  | P(CC₃1−2a)        | −25.939 | −26.704 | −22.225 |
|                      | P(CC₃1−2b)        | −42.204 | −45.058 | −39.165 |
| (Ph)₂POCH₃+CCl₃PO(OEt)₂ | P(CC₃1−2b)    | −14.843 | −15.845 | −12.001 |
|                      | P(CC₃1−2b)        | −46.238 | −47.081 | −44.397 |

Fig. 3 Bond lengths for the transition states of the reaction of (EtO)₃P and (Ph)₂POCH₃ to the reagents CCl₃PO(OEt)₂ and CCl₃PO(Ph)₂
Global reactivity indices are an efficient tool for the analysis and prediction of the polar or non-polar character of such reactions [22–24]. The density functional theory (DFT) is currently a real source of chemical concepts such as electronic chemical potential $\mu$ and hardness $\eta$. From these two global descriptors, other indices such as the global softness $S$ or the global electrophilic index $\omega$ can be evaluated. These indices are calculated from the energies of the lowest vacant and highest occupied Kohn-Sham orbitals. It has been shown that the nucleophilicity of a molecule can be related to its ability to neglect its electron density [25]. The nucleophilicity index $N$ can be calculated by the following equation [22]:

$$N = E_{\text{LUMO}}(\text{Nu}) - E_{\text{HOMO}}(\text{TCE})$$

- $E_{\text{HOMO(TCE)}}$ is the HOMO energy of tetracyanoethylene (TCE).
- $E_{\text{LUMO(Nu)}}$ is the LUMO energy of the nucleophile.

According to results presented in Table 1, the two trivalent phosphorus derivatives have the lowest electrophilicity index $\omega_{(\text{EO})_3\text{P}} = 0.640 \text{ eV}$ and $\omega_{(\text{Ph})_2\text{POCH}_3} = 1.180 \text{ eV}$ compared to polyhaloalkanes

$$[(\omega_{\text{CCl}_3\text{PO(OEt)}}_1 = 1.727 \text{ eV and } \omega_{\text{CCl}_3\text{PO(Ph)}}_1 = 1.881 \text{ eV}]],$$

and the highest nucleophilicity index

$$[(N_{(\text{EO})_3\text{P}} = 2.428 \text{ eV and } N_{(\text{Ph})_2\text{POCH}_3} = 3.237 \text{ eV}]].$$

In addition, the electronic chemical potential of the reagents $(\text{EtO})_3\text{P}$ and $(\text{Ph})_2\text{POCH}_3$ is at a higher energy level than polyhalogénoalkanes $\text{CCl}_3\text{PO(OEt)}_2$ and $\text{CCl}_3\text{PO(Ph)}_2$.

In conclusion, the three theoretical approaches (gaps HOMO/LUMO, the values of the electronic chemical potentials, and the values of the electrophilic (nucleophilic) indices) show that the two polyhaloalkanes act as electrophiles (electron acceptor) while the trivalent phosphorus compounds act as nucleophiles (electron donor).

The difference in electrophilicity ($\Delta\omega$) between the electrophile and the nucleophile is high in the case of triethylphosphate $(\text{EtO})_3\text{P}$. It is also observed that the nucleophilic character is increased by the presence of substituents (–Ph); this shows that the reaction of diethyltrichloromethyl phosphonate $\text{CCl}_3\text{PO(OEt)}_2$ with $\text{POCH}_3$ is more favorable than with $(\text{EtO})_3\text{P}$.

### Analysis of local properties

In order to differentiate the reactivity of the atoms forming a molecule, the local indices, in this case the Parr functions $\text{Parr}^+(r)/\text{Parr}^-(r)$, were calculated. Table 2 summarizes the values of the local descriptors of reactivity obtained by the method DFT/B3LYP/6-311G(d,p). According to the results obtained, the most favored electrophilic-nucleophilic interaction is between the carbon atom of diethyl trichloromethyl phosphonate $\text{CCl}_3\text{PO(OEt)}_2$ and the chlorine halogen of trichloromethyl phosphine oxide $\text{CCl}_3\text{PO(Ph)}_2$ and the phosphorus atom which acts as nucleophilic site of trivalent phosphorus derivatives.

### Thermodynamic study

The reaction of diethyltrichloromethyl phosphonate $\text{CCl}_3\text{PO(OEt)}_2$ with phosphorus compounds $[\text{P(OEt)}_3$ and $(\text{Ph})_2\text{POCH}_3]$ and the reaction of trichloromethyl phosphine oxide $\text{CCl}_3\text{PO(Ph)}_2$ with triethylphosphate $\text{P(OEt)}_3$ were studied according to Fig. 1. Using the calculation method DFT/B3LYP/6-311G(d,p), we have calculated and reported in Table 3 the variations in reaction energy $\Delta E_r$, the variations in reaction enthalpy $\Delta H_r$, and the variations in free reaction enthalpy $\Delta G_r$ which correspond to the formation reactions of the products $\text{PC}$ and $\text{PCl}$. Our ultimate goal is to understand the effect of substitution of the ethoxy (–OEt) group by a phenyl (–Ph) group on the reactivity of our systems.

Table 3 shows that the negative values of the free enthalpy variations $\Delta G_r$ prove that these reactions are possible and thermodynamically favored. On the other hand, the absolute values of the free enthalpy of reaction variation $\Delta G_r$ that correspond to the formation reactions of $\text{PC}$ compounds from the attack on the chlorine halogen are higher than those of the free enthalpy of reaction variation that correspond to the formation reactions of $\text{PC}$ compounds from the attack on the carbon $\text{C}$ atom. This result shows that $\text{PC}$ compounds are more thermodynamically stable than $\text{PC}$ compounds, which indicate that the attack on the chlorine atom is the most favorable. Moreover, we noticed that the reaction leading to $\text{PC}(1b−2a)$ is more favored thermodynamically than the other reactions, since we found a higher absolute value of free enthalpy of reaction. Consequently, the substitution of the ethoxy (–OEt) group by a phenyl (–Ph) group favors the attack on the chlorine atom.

Results also show that the values of $\Delta H_r$ and $\Delta G_r$ of the formation reactions of the compounds $\text{PC}$ and $\text{PCl}$ are negative. Therefore, they are exothermic.

We also noted that the absolute values of $\Delta E_r$, which correspond to the formation reactions of the compounds $\text{PC}(1a−2a)$, $\text{PC}(1a−2b)$, and $\text{PC}(1b−2a)$ are more important than those of the formation reactions of compounds $\text{PCl}(1a−2a)$, $\text{PCL}(1a−2b)$, and $\text{PCL}(1b−2a)$. This confirms again that the most favorable site of attack is the chlorine atom.

We can conclude from this theoretical study that the two nucleophilic modes of attack $(\text{A}_P(\text{EtA}_C)_1)$ of phosphinite $(\text{Ph}_2\text{POCH}_3)$ on diethyltrichloromethyl phosphonate $\text{CCl}_3\text{PO(OEt)}_2$ and phosphite $(\text{EtO})_3\text{P}$ on both electrophiles $\text{CCl}_3\text{PO(OEt)}_2$ and $\text{CCl}_3\text{PO(Ph)}_2$ are thermodynamically
possible and the products from the attack on the chlorine atom are thermodynamically more favored.

**Kinetic study**

**Transition state and activation barrier**

The transition state theory (TST) will obviously be used to predict the experimentally observed regioselectivity. We remember that according to this theory, the passage from reagents (initial state) to products (final state) requires the passage through a transition state (intermediate state).

In order to highlight the type of nucleophilic attack of the phosphorus atom of organophosphorus compounds (EtO)₃P and (Ph)₂POCH₃ on the most electrophilic center of polyhaloalkanes CCl₃PO(OEt)₂ and CCl₃PO(Ph)₂ (Aₜ and A_Cl), the release of an activation barrier is necessary to reach the final state. The transition states (TSs), corresponding to the two attack modes A_tC and A_Cl, have been located at the level of calculation B3LYP/6-311G(d,p) whose results are summarized in Table S5. These TSs were confirmed by the presence of one and only one imaginary frequency in the Hessian matrix.

In this part of our work, we have shown that the attack on the chlorine A_Cl atom is kinetically more favorable considering the very high value of the ratio of the velocity constants of the two nucleophilic attack modes (K_C/K_Cl).

**Structural study of transition states**

The structures optimized by the DFT/B3LYP/6-311G(d,p) method, the TS (transition state) states of the reaction of diethyltrichloromethyl phosphonate CCl₃PO(OEt)₂ with phosphorus compounds [P(OEt)₃ and (Ph)₂POCH₃], and the reaction of trichloromethyl phosphine oxide CCl₃PO(Ph)₂ with triethyl phosphate P(OEt)₃ are presented in Fig. 3. The analysis of the results obtained shows that the structure of the transition state associated with the A_C attack mode is less stable than that associated with the A_Cl attack mode. Phosphite is therefore more reactive with chlorine halogen than carbon atom because the length of the P − CCl₂ bond is less than that of the P − Cl one in the transition state.

**Determination of the reaction path**

The evolution of the molecular system along the reaction path between diphenyl methyl phosphinite (Ph)₂POCH₃ and diethyltrichloromethylphosphonate CCl₃PO(OEt)₂ and between the triethylphosphate (EtO)₃P and the polyhaloalkanes CCl₃PO(OEt)₂ and CCl₃PO(Ph)₂ has been studied to ensure that the transition states determined are correct. The intrinsic reaction coordinate (IRC) calculation shown in Fig. S3 should ensure that the transition state is related to the reagent and product minima.

**Conclusions**

The calculations of the global indices and the gap_{PLUMO-HOMO} by the quantum method DFT/B3LYP/6-311G(d,p) show that the (EtO)₃P and (Ph)₂POCH₃ reagents behave as nucleophiles and that the polychloroalkanes CCl₃PO(OEt)₂ and CCl₃PO(Ph)₂ act as electrophiles.

Using population analyses MPA and NPA, the calculation of partial atomic charges shows that the chlorine halogen is an electrophilic center. It is reminded that the calculation of net charges provided us with good predictions. Nevertheless, it is known in the literature that the calculation of net charges is not considered to be a sufficient descriptor for the prediction of attack sites. To overcome this problem, Parr functions were calculated using the population analysis NPA. The results thus obtained show that the chlorine halogen of CCl₃PO(Ph)₂ and the carbon atom of CCl₃PO(OEt)₂ should behave as the most reactive sites against nucleophilic attack and the phosphorus atom of trivalent phosphorus derivatives should act as the most nucleophilic site.

The thermodynamic and kinetic studies show that the stable products are those obtained from the attack on the chlorine halogen. The substitution of the ethoxy (−OEt) group by a phenyl (−Ph) group favors the attack on the chlorine atom.

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**Availability of data and material** All data generated or analyzed during this study are included in this published article.

**Code availability** The calculations were performed using Gaussian 09W and GaussView 5.0 provided by Gaussian 09 and GaussView 05.

**Author contribution** Ali Barhoumi, Mohammed El Idrissi, and Abdessamad Tounsi: article writing. Salam Bakkas and Abdeslam El Hajbi: directing, discussion. Mohammed El Idrissi and Abdellah Zeroual: final review and editing.

**Declarations**

**Ethics approval** The manuscript is prepared in compliance with the Ethics in Publishing Policy as described in the Guide for Authors.

**Consent to participate** The manuscript is approved by all authors for publication.

**Conflict of interest** The authors declare no competing interests. }

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