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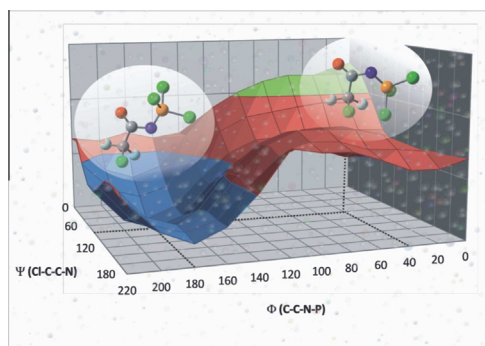
Synthesis, spectroscopic characterization and theoretical calculations of $\text{ClF}_2\text{CC}(\text{O})\text{N}=\text{PCl}_3$ ([chloro(difluor)acetyl]phosphorimidic trichloride)

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HIGHLIGHTS

- The novel compound $\text{ClF}_2\text{CC}(\text{O})\text{N}=\text{PCl}_3$, was prepared and characterized.
- Vibrational properties were investigated by using experimental and theoretical approach.
- The results indicate a C_1 form in the liquid, with $\text{C}=\text{O}$ bond in *syn* position with respect to the $\text{P}=\text{N}$ bond.
- The calculated wavenumbers were fitted according to the Wavenumber-Linear-Scaling Method.

GRAPHICAL ABSTRACT



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ABSTRACT

The synthesis of [chloro(difluor)acetyl]phosphorimidic trichloride ($\text{ClF}_2\text{CC}(\text{O})\text{N}=\text{PCl}_3$), together with a tentative assignment of the vibrational, NMR and mass spectra, are reported. Quantum chemical calculations (MP2 and B3LYP methods with 6-311+G(d) and 6-311+G(2df,p) basis sets) predict three stable conformers in the gas phase (*syn*, *gauche* and *anti*, defined according to the rotation around both the $\text{Cl}-\text{C}-\text{N}$ and the $\text{C}-\text{C}-\text{N}-\text{P}$ dihedral angles). However, only a single C_1 symmetry conformer is observed in the liquid phase, possessing the $\text{C}=\text{O}$ double bond in *synperiplanar* orientation with respect to the $\text{P}=\text{N}$ double bond, and the $\text{Cl}-\text{C}$ bond distorted from the plane defined by the $\text{CC}(\text{O})\text{NP}$ entity. A Natural Bond Orbital (NBO) analysis was carried out for the title compound and related molecules in order to provide an explanation about the electronic properties.

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Introduction

The structural and vibrational analysis of compounds with phosphorus–nitrogen backbones has been our topic of interest for the last years [1–4]. The ascertainment of the molecular spatial arrangement is very important, for boosting the development of materials with useful characteristics as in polymer, pharmaceuticals and industrial chemistry. For instance, the phosphazenes (which have alternating $\text{P}=\text{N}$ groups into the backbone) have proved to

be excellent additives to organic polymers [5] and have also helped in transforming them into useful flame-retardants [6]. In particular, species containing the $\text{N}=\text{PCl}_3$ entity play a significant role in macromolecular substitution reactions producing organic and inorganic polymers with useful properties [7]. $\text{CF}_3\text{C}(\text{O})\text{N}=\text{PCl}_3$ [1] and $\text{CCl}_3\text{C}(\text{O})\text{N}=\text{PCl}_3$ [1] were also used as reactants in the synthesis of N-carbacylamidophosphate compounds, $\text{CCl}_3\text{C}(\text{O})\text{NHP}(\text{O})\text{Cl}_2$ [2] and $\text{CF}_3\text{C}(\text{O})\text{NHP}(\text{O})\text{Cl}_2$ [2,8], which possess interesting properties as O,O'-donor ligands for metal ions [9–12].

In our previous studies, the vibro-conformational properties of a series of monophosphazene compounds, i.e. $\text{ClSO}_2\text{N}=\text{PCl}_3$ [13], $\text{CF}_3\text{C}(\text{O})\text{N}=\text{PCl}_3$, $\text{CCl}_3\text{C}(\text{O})\text{N}=\text{PCl}_3$, and $\text{CF}_3\text{SO}_2\text{N}=\text{PCl}_3$ [4], were

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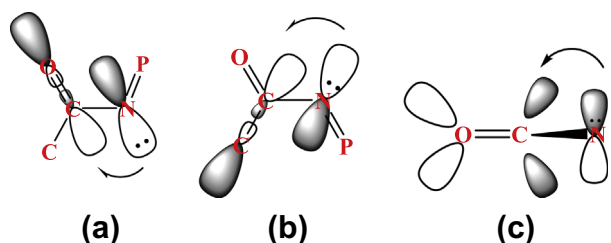


Fig. 1. Orbital interactions according to the NBO analysis. Delocalizations from the lone pair of the nitrogen to (a) $\sigma_{C=O}^*$, (b) $\pi_{C=O}^*$ and (c) $\pi_{C=N}^*$.

investigated on the basis of infrared and Raman spectra, and theoretical calculations performed at different levels of theory. For all the compounds, only one stable form was experimentally observed in both the liquid and solid phases. On the contrary, theoretical calculations predict two stable conformations (*syn* and *anti*), defined according to the relative position of C=O (or S=O) bond with respect to N=P bond. Each particular arrangement allows different electronic interactions – called anomeric and mesomeric –, which act stabilizing the conformations. In Fig. 1 are depicted the anomeric (a and b) and mesomeric (c) delocalizations.

The calculated data for the perfluoroacetylated compound (i.e. $CF_3C(O)N=P(Cl)_3$), gave two stable conformers in the gas phase defined as *syn* and *anti* forms, depending on the relative position of the C=O and P=N groups. The conformer corresponding to the lowest electronic energy shows C_1 symmetry and possesses a *syn* conformation with a dihedral angle $\phi_{CCNP}=180^\circ$. Additional information supplied by the NBO analysis [14], led us to conclude that the C=O and P=N groups lay opposite to each other in the same plane, allowing ya dijimos antes que eran importantes anomeric and mesomeric delocalizations [15–18] to take place. In fact, it has been demonstrated that these interactions largely contribute to the total stabilization energy, through delocalizations from the lone pair located on the nitrogen atom to the $\sigma_{C=O}^*$, $\sigma_{C=N}^*$ (anomeric) and $\pi_{C=O}^*$ (mesomeric) orbitals (see Fig. 1).

For $CCl_3C(O)N=P(Cl)_3$, no-scan around the C–N bond could be done, because the steric repulsion arising from the presence of two bulky end groups (such as CCl_3 and $P(Cl)_3$). For that reason, all the optimizations had to be performed for three fixed conformations, i.e. *syn*, *gauche* and *anti*. According to the calculus, the *syn* form corresponds to the structure with the lowest electronic energy, strongly favored by the electronic delocalizations.

Recently we reported the synthesis and FT-IR, Raman and mass spectra of a new compound, [chloro(difluoro)acetyl]phosphoramidic acid dichloride ($CClF_2C(O)NHP(O)Cl_2$ [3]) obtained from hydrolysis of $CClF_2C(O)N=P(Cl)_3$. It was found as a dimer in the solid phase, with the C=O double bond in *anti* position relative to the P=O double bond. Unlike what occurs to $CCl_3C(O)NHP(O)Cl_2$ and $CF_3C(O)NHP(O)Cl_2$ –where remarkable interactions between the σ_{C-X}^* and $\pi_{C=O}^*$ ($X = Cl, F$) orbitals are present –, the NBO analysis showed complete absence of electronic delocalizations, revealing that the behavior of the $CClF_2$ group is mainly dominated by the electronic repulsions, as occurs to $CCl_2FC(O)NH_2$ (CDFA) [19].

Taking into account the the scarcity of data about the performance of the perhalogenated monophosphazene compounds, we have synthesized the title compound and analyzed its vibrational spectra and the electronic effects responsible for its conformational properties, both experimentally and theoretically. The study of $CClF_2C(O)N=P(Cl)_3$ increases the knowledge about the series of monophosphazenes reported so far.

Experimental

Chemical synthesis

Commercial samples of $ClF_2CC(O)NH_2$ (Fluka, 98%) and phosphorus pentachloride in equimolar amounts were placed in a reaction flask and allowed to react at reflux at $80^\circ C$ in CCl_4 for 2 h. The reaction was carried out under nitrogen atmosphere. Special care has been taken to prevent the reaction with air moisture [1]. The solvent was completely evaporated in vacuum and the remaining liquid distilled under nitrogen atmosphere. The neat compound was obtained in the $41^\circ C$ fraction and its purity was confirmed by GC–Mass spectrometry.

In order to seek for improvements and to perform a more sustainable chemical synthesis, a new method using microwave heating without solvents was probed. In a dry box under nitrogen atmosphere, equimolar amounts of CDFA and $P(Cl)_5$ (6 mmol) were placed in a 30 mL vial. The reaction was complete after 20 min at $110^\circ C$; nevertheless the yield was rather low ($\sim 20\%$). Higher yields were obtained adding 1 mL of dry CCl_4 to form a slurry that allows an intimate contact between the two solids. With a milder heating ($80^\circ C$ for 20 min) the yield rose to 86%.

Material and methods

The infrared spectra between 4000 and 400 cm^{-1} (resolution 2 cm^{-1}) were recorded with a Perkin Elmer 1600 series FTIR, by placing the sample between NaCl plates.

Raman spectra between 3500 and 150 cm^{-1} were recorded using a DXR Smart Raman Spectrometer (spectral resolution 2 cm^{-1}). The 780-nm radiation line was used for excitation. The solid samples were handled in Pyrex capillaries at room temperature. 1H , ^{13}C , and ^{31}P NMR spectra were recorded with a Bruker Avance II 400 MHz spectrometer. The spectra were measured at room temperature using 5-mm o.d. probes. $CDCl_3$ was used as solvent and referenced internally to $(CH_3)_4Si$ for 1H and ^{13}C NMR, while for ^{31}P NMR the spectra were compared with H_3PO_4 85% as external reference.

Gas chromatography/MS (GC/MS) analysis was performed in a Shimadzu GC–MS–QP 5050 spectrometer equipped with a VF column ($30\text{ m} \times 0.25\text{ mm} \times 5\text{ }\mu\text{m}$), using helium as eluent at a flow rate of 1.1 mL/min. The injector and ion source temperature was

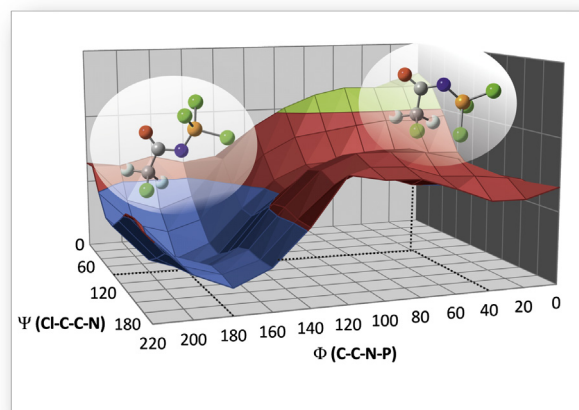


Fig. 2. Potential energy surface, and *syn* and *anti* conformations of the minima for $CClF_2C(O)N=P(Cl)_3$, calculated at B3LYP/6-311+G(2df,p) level.

280 °C, the oven heating ramp was 15 °C/min from 50 °C up to 280 °C and the interface temperature was 280 °C. The pressure in the MS instrument was 10^{-5} mbar, precluding ion–molecule reactions from taking place, and MS recordings were made in the electron impact mode (EI) at an ionization energy of 70 eV.

Reactions under microwave irradiation were performed in cylindrical quartz tubes ($\phi = 1.5$ cm) placed in a CEM microwave reactor (2.455 GHz), with adjustable power within the range 0–300 W and a wave guide (monomode) fitted with a stirring device and an IR temperature detector.

Quantum chemical calculations

The potential energy surface (PES) was analyzed by structure optimizations at fixed values of the torsional angles Cl–C–C–N and C–C–N=P in steps of 20° using *ab initio* (HF/6-31G(d)) and hybrid (B3LYP) methods with 6-311G(d) and 6-311+G(2df,p) basis sets (see Fig. 2) under the Gaussian 09 program suite [20].

The electronic delocalizations of the most stable conformer were rationalized by a Natural Bond Orbital analysis (NBO) [14], using the hybrid method B3LYP with 6-311G(d) basis set.

Results and discussion

Conformational analysis

CF₃C(O)NPCI₃ and CCl₃C(O)NPCI₃ molecules have been described as having an almost planar configuration around the CCNP dihedral angle, and two electronic delocalizations, namely anomeric and mesomeric. Since our interest is mainly focused in acquiring a complete understanding of the geometries and stabilities of compounds possessing the –N=PCl₃ entity, we consider very appropriate to invoke the results reported for ClSO₂N=PCl₃ [13] and CF₃SO₂N=PCl₃ [4]. Both molecules exist as a single form according to the experimental vibrational spectra, also in agreement with the calculated results. A *syn* orientation of one of the S=O bonds respect to the N=P group is found for both compounds, and one of the P–Cl bonds being in nearly *anti* position with respect to the N–S bond.

The PES of ClF₂CC(O)N=PCl₃, performed at B3LYP level of approach, presents two minima. The local minimum found for dihedral angles of $\phi(\text{CCNP}) \approx 40^\circ$ and $\Psi(\text{CICCN}) \approx 85^\circ$, correspond to the anti conformer, while the global minimum found for dihedrals $\phi(\text{CCNP}) \approx 180^\circ$ and $\Psi(\text{CICCN}) \approx 80^\circ$ belong to the *syn* conformer. The energy difference between them is 3.32 kcal/mol, thus it is expected that in fluid phases at room temperature, only the *syn* conformer will be present.

In Fig. 2, the PES together with the conformers corresponding to each minimum is shown. The geometric parameters for the fully optimized *syn* structure obtained by two computational methods are collected in Table 1. A good correlation is observed between both MP2 and B3LYP approaches, not only for the angles but also for the bond distances.

Theoretical prediction of the vibrational spectrum

Improvements in the calculated wavenumbers with basis set size, as well as the use of scale factors, is well established [21]. In this work, we applied the Wavenumber–Linear–Scaling Method (WLS) [22], which is based on the straightforward relationship between the scale factor and the vibrational wavenumbers. This factor is the ratio $v_{\text{exp}}/v_{\text{calc}}$, calculated through the linear equation $v_{\text{exp}}/v_{\text{calc}} = 1.0087(9) - 0.0000163(6)v_{\text{calc}}$, proposed by Yoshida [22]. Fig. 3 shows four curves, corresponding to calculated vs experimental wavenumbers, for the B3LYP and HF method. In

Table 1

Geometrical calculated parameters for the *syn* conformer of ClF₂CC(O)N=PCl₃. Bond lengths in Å and angles in degrees.

	MP2 6-311+G(2df,p)	B3LYP	
		6-31G(d)	6-311G(d)
C–Cl	1.769	1.806	1.335
F–C ^a	1.335	1.340	1.339
C–C	1.540	1.552	1.553
C–O	1.215	1.213	1.204
C–N	1.372	1.379	1.376
N–P	1.556	1.561	1.548
P–Cl ^a	1.995	2.029	2.036
Cl–C–C	108.9	109.4	109.6
F–C–C ^a	110.6	110.6	110.6
F–C–Cl ^a	109.3	108.8	108.8
F–C–F	108.3	108.6	108.2
C–C–O	120.3	120.0	120.2
C–C–N	111.1	111.7	111.3
O–C–N	128.6	128.3	128.4
C–N–P	119.6	124.1	127.1
N–P–Cl ^a	113.9	112.6	114.3
P–N–C=O	1.576	1.3	0.0
Cl–C–C=O	–105.3	–98.6	–104.8
F–C–C=O	14.7	20.7	15.2
C–C–N–P	–177.3	–178.1	–179.7

^a Mean values are given for parameters that are not unique.

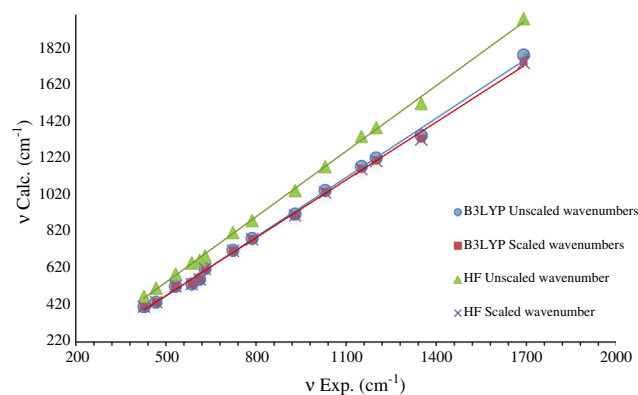


Fig. 3. Plot of calculated vs experimental wavenumbers (with and without scaling). B3LYP method was performed with 6-311G(d), and HF with 6-31G(d) basis set.

Table 2 are reported the experimental and calculated wavenumbers, the WLS-scale factor and the corrected frequencies.

The wavenumbers obtained as result of applying the WLS method to DFT calculated spectra fit very well with a linear curve, as should be expected [23,24]. However, in our case, there is an additional paramount use, which is its application to wavenumbers calculated with the simplest HF level of theory. The set of fitted frequencies presented in the figure were obtained using 6-31G(d) basis set, which implies a very low computational cost for molecules of the size as ClF₂C(O)NPCI₃. In the figure, the unscaled HF frequencies are represented by triangular symbols, showing a noticeable shifting from the curves corresponding to scaled and unscaled B3LYP method (see Fig. 3). Nonetheless, when they are scaled, the frequencies values fall much closer to the DFT curves (B3LYP/6-311+G(2df,p)). This means that it is possible to use very low cost methods to obtain reliable values after scaling, which implies a substantial improvement in the calculated spectra.

NBO analysis

In a previous work [1], results obtained from the NBO program were used to rationalize the preference of CF₃C(O)NPCI₃ and CCl₃.

Table 2Experimental, calculated, WLS-scale factor and scaled wavenumbers of $\text{ClF}_2\text{C}(\text{O})\text{N}=\text{PCl}_3$.

$\nu_{\text{Exp.}}$	$\nu_{\text{Calc.}}^a$	WLS-scale factor	ν_{WLS}
1691	1781	0.97967	1745
1350	1343	0.98681	1325
1200	1221	0.98880	1207
1151	1175	0.98955	1162
1030	1044	0.99168	1035
930	916	0.99377	910
787	783	0.99594	780
723	719	0.99698	717
630	619	0.99861	618
612	562	0.99954	562
586	536	0.99996	536
532	524	1.00016	524
467	437	1.00158	438
427	412	1.00198	413

^a (B3LYP/6-311+G(d)).**Table 3**Total energy (ΔE_{total}) and stabilization energies of the mesomeric and anomeric effect (kcal/mol) calculated for both *syn* and *anti* conformations of $\text{ClF}_2\text{C}(\text{O})\text{N}=\text{PCl}_3$.

	$\text{Lp}_\text{N} \rightarrow \sigma_{\text{C}=\text{O}}^*$	$\text{Lp}_\text{N} \rightarrow \sigma_{\text{C}-\text{C}}^*$	$\text{Lp}_\text{N} \rightarrow \pi_{\text{C}=\text{O}}^*$
Syn	9.92	1.77	59.15
Anti	3.99	10.69	50.69
ΔE_{Anom}	-2.99		
ΔE_{Mesom}	8.46		
ΔE_{total}	5.47		

 $\Delta E_{\text{Anom}} = \text{Anom}_{\text{syn}} - \text{Anom}_{\text{anti}}$ $\Delta E_{\text{Mesom}} = \text{Mesom}_{\text{syn}} - \text{Mesom}_{\text{anti}}$ **Table 4**Orbital description and stabilization energies (kcal/mol) of $\text{CF}_3\text{C}(\text{O})\text{N}=\text{PCl}_3$, $\text{CClF}_2\text{C}(\text{O})\text{N}=\text{PCl}_3$ and $\text{CCl}_3\text{C}(\text{O})\text{N}=\text{PCl}_3$ (X = F or Cl).

Orbitals	Stabilización energies (kcal/mol)		
	$\text{CF}_3\text{C}(\text{O})\text{N}=\text{PCl}_3$	$\text{CClF}_2\text{C}(\text{O})\text{N}=\text{PCl}_3$	$\text{CCl}_3\text{C}(\text{O})\text{N}=\text{PCl}_3$
$\text{Lp}_\text{N} \rightarrow \pi_{\text{CO}}^*$	57.90	59.15	59.59
$\text{Lp}_\text{N} \rightarrow \sigma_{\text{CX}}^*$	0.53	–	0.64
$\sigma_{\text{C}-\text{X}} \rightarrow \pi_{\text{CO}}^*$	1.67	2.98	4.71

^a Mean values.

$\text{C}(\text{O})\text{N}=\text{PCl}_3$ for the *syn* conformation. Two relevant interactions - called anomeric and mesomeric effects - were described as donor \rightarrow acceptor delocalization's type. Historically, the anomeric effect was formulated as an effective strategy to explain structures, properties and reactivity of cyclic oxygen-containing carbohydrates, particularly sugars [25]; and the mesomeric delocalization was described as the most relevant factor in determining the

Table 5¹³C, ¹⁹F and ³¹P NMR chemical shifts and coupling constants of $\text{ClF}_2\text{C}(\text{O})\text{N}=\text{PCl}_3$, $\text{F}_3\text{C}(\text{O})\text{N}=\text{PCl}_3$ and $\text{Cl}_3\text{C}(\text{O})\text{N}=\text{PCl}_3$.

	$\text{ClF}_2\text{C}(\text{O})\text{N}=\text{PCl}_3$				$\text{F}_3\text{C}(\text{O})\text{N}=\text{PCl}_3$				$\text{Cl}_3\text{C}(\text{O})\text{N}=\text{PCl}_3$			
	¹³ C NMR		¹⁹ F NMR	³¹ P NMR	¹³ C NMR		¹⁹ F NMR	³¹ P NMR ^d	¹³ C NMR		¹⁹ F NMR	³¹ P NMR ^d
	CO	ClF_2C			CO	F_3C			CO	Cl_3C		
δ^a	163.7	118.7	-64.2	28.7	161.7	115.4	-70.95	26.1	165.7	94.2	22.5	
m^b	dt	t	d	s	dq	dq	d	s	d	d	s	
J^c	$^2J_{\text{CF}} = 33$	$^2J_{\text{CP}} = 13$	$^1J_{\text{CF}} = 302$	$^4J_{\text{FP}} = 8$	$^2J_{\text{CF}} = 40$	$^2J_{\text{CP}} = 13$	$^1J_{\text{CF}} = 287$	$^3J_{\text{CP}} = 46$	$^4J_{\text{FP}} = 10$	$^2J_{\text{CP}} = 12$	$^3J_{\text{CP}} = 44$	

^a $\delta(^{13}\text{C})$ in ppm relative to TMS in CDCl_3 , $\delta(^{19}\text{F})$ in ppm relative to 0.05% TFA in chloroform-d ($\delta = -71.0$ ppm) as external reference. $\delta(^{31}\text{P})$ in ppm relative to H_3PO_4 85% as external reference.^b Signal multiplicities: s = singlet, d = doublet, t = triplet, dt = double triplet, dq = double quartet.^c Coupling constant values in Hz.^d These values were re-assigned.

structure and conformation of acetamide derivative compounds [19,26]. More recently, the same concept was extended to many other compounds. It was also proved that the anomeric effect operates equally effectively in both acyclic and cyclic compounds containing atoms with lone pairs, such as N, O and S [15,18,27–29].

Table 3 lists the anomeric (represented by the $\text{Lp}_\text{N} \rightarrow \sigma_{\text{C}=\text{O}}^*$ and $\text{Lp}_\text{N} \rightarrow \sigma_{\text{C}-\text{C}}^*$ delocalizations) and mesomeric (by $\text{Lp}_\text{N} \rightarrow \pi_{\text{C}=\text{O}}^*$ interaction) effect values for both *anti* and *syn* conformations of the title compound. The *syn* spatial arrangement adopted by the molecule is strongly supported by the mesomeric interaction ($\Delta E_{\text{Mesom}} = 8.46$ kcal/mol) though for many other compounds it is usually the anomeric effect the one that dictates the geometry. The total energy gained from delocalization effects is 5.47 kcal/mol.

The magnitude of the electronic delocalizations of $\text{CClF}_2\text{C}(\text{O})\text{N}=\text{PCl}_3$ and of related molecules will be used to understand some particular modes of vibration. For this reason, the results of the NBO analysis of $\text{CF}_3\text{C}(\text{O})\text{N}=\text{PCl}_3$, $\text{CCl}_3\text{C}(\text{O})\text{N}=\text{PCl}_3$ and $\text{CClF}_2\text{C}(\text{O})\text{N}=\text{PCl}_3$ are presented in Table 4, and will be discussed when appropriate.

NMR measurements

Table 5 shows the chemical shifts (δ , ppm), multiplicity and coupling constants (J , Hz) for the title compound and some closely related molecules, i.e. $\text{CF}_3\text{C}(\text{O})\text{N}=\text{PCl}_3$ and $\text{CCl}_3\text{C}(\text{O})\text{N}=\text{PCl}_3$ [1]. It is important to mention that the shift in the ³¹P assignment of $\text{CF}_3\text{C}(\text{O})\text{N}=\text{PCl}_3$ and $\text{CCl}_3\text{C}(\text{O})\text{N}=\text{PCl}_3$ can be substantially improved on account of previous data for $\text{CClF}_2\text{C}(\text{O})\text{N}=\text{P}(\text{O})\text{Cl}_2$ [3], $\text{CF}_3\text{C}(\text{O})\text{N}=\text{P}(\text{O})\text{Cl}_2$ [2] and $\text{CCl}_3\text{C}(\text{O})\text{N}=\text{P}(\text{O})\text{Cl}_2$ [2] and the present measurements as will be shown below.

According to the ¹³C spectra, the shift of the C(O) group does not suffer a significant change suggesting a scarce influence of the $\text{N}=\text{PCl}_3$ group on the carbonyl behavior. There is only a slight deshielding (~ 2 ppm) on each step when going from $\text{CF}_3\text{C}(\text{O})\text{N}=\text{PCl}_3$ to $\text{CClF}_2\text{C}(\text{O})\text{N}=\text{PCl}_3$ and $\text{CCl}_3\text{C}(\text{O})\text{N}=\text{PCl}_3$. This shift, as well as the shift occurring at the C atom directly bonded to the halogen atoms, could be ascribed to the resonance effect which is perturbed by the substitution and the subsequent change in conformation of the molecule. In fact, the totally fluorinated presents the *syn* conformation (with the dihedral angle described around the C–C bond) as the most stable, while for the totally chlorinated one, the stable conformer is *anti*, and for partial substitution the preferred structure is *gauche*. This means that for $\text{CF}_3\text{C}(\text{O})\text{N}=\text{PCl}_3$ the dihedral F–C–C=O is planar and the resonance deshields the carbonyl and increases the shielding on the terminal C atom. When one fluor atom is substituted by Cl, the change in structure prevents the F–C–C=O dihedral to be planar, difficulting the resonance with the result of a carbonyl group more shielded and a terminal group more deshielded. When all F atoms are replaced by Cl, there is no resonance at all and only the decrease in electronegativity of the substituents takes over.

Table 6Experimental and calculated wavenumbers of $\text{ClF}_2\text{CC}(\text{O})\text{N}=\text{PCl}_3$, and approximate assignment of observed normal modes of vibration.

Approximate description ^a	Experimental ^b						Calculated ^c						
	IR (cm^{-1})		Raman (cm^{-1})		MP2/6-311+G(2df,p) ^d		B3LYP/6-311G(d)		B3LYP/6-311+G(2df,p)				
$\nu \text{C}=\text{O}$	1691	vs	1695	(28)	1702	(62)	(100)	1781	(45)	(32)	1753	(46)	(65)
$\nu \text{P}=\text{N}$	1350	vs	1353	(6)	1346	(100)	(67)	1343	(100)	(100)	1346	(100)	(100)
$\nu_s \text{CF}_2$	1200	s	1198	(7)	1209	(69)	(25)	1221	(56)	(16)	1210	(54)	(22)
$\nu_{as} \text{CF}_2$	1151	m	1167	(5)	1168	(99)	(17)	1175	(20)	(3)	1155	(19)	(4)
$\nu \text{C}-\text{C}$	1030	s	1029	(21)	1045	(28)	(33)	1044	(13)	(3)	1037	(10)	(48)
$\nu \text{C}-\text{Cl}$	930	s	937	(12)	939	(16)	(50)	916	(19)	(22)	915	(17)	(26)
$\nu \text{C}-\text{N}$	787	s	784	(29)	789	(22)	(67)	783	(12)	(42)	783	(12)	(4)
$\rho \text{C}=\text{O}$	723	m	712	(6)	722	(35)	(33)	719	(23)	(13)	720	(21)	(13)
δCClF_2	630	m	628	(32)	626	(14)	(17)	619	(6)	(6)	621	(5)	(22)
$\nu_{as} \text{PCl}_3$	612	s	610	(20)	607	(27)	(33)	562	(22)	(16)	581	(20)	(61)
$\nu_{as} \text{PCl}_3$	586	s	593	(23)	589	(33)	(50)	536	(28)	(55)	561	(24)	(43)
ωCClF_2	532	w	532	(83)	533	(6)	(92)	524	(3)	(39)	527	(3)	(43)
$\nu_s \text{PCl}_3$	467	m	466	(59)	467	(8)	(58)	437	(9)	(39)	449	(7)	(17)
δCClF_2	427	vw	427	(100)	426	(<1)	(50)	412	(<1)	(39)	415	(<1)	(22)
$\delta \text{C}=\text{O}$	-	-	362	(24)	357	(<1)	(33)	357	(<1)	(16)	356	(<1)	(17)
ρCClF_2	-	-	338	(22)	334	(<1)	(42)	325	(<1)	(29)	329	(<1)	(22)
τCClF_2	-	-	323	(41)	324	(<1)	(25)	318	(<1)	(19)	319	(<1)	(9)
δPCl_3	-	-	300	(60)	291	(<1)	(42)	392	(<1)	(19)	292	(<1)	(9)
ωPCl_3	-	-	252	(35)	248	(<1)	(33)	242	(<1)	(19)	244	(<1)	(9)
τPCl_3	-	-	212	(31)	209	(<1)	(25)	206	(<1)	(19)	205	(<1)	(2)
δPCl_3	-	-	181	(79)	176	(<1)	(25)	173	(<1)	(10)	172	(<1)	(6)

^a ν = stretching, δ = deformation, ρ = rocking, τ = twisting, ω = wagging, s = symmetric, as = asymmetric.^b vs = very strong, s = strong, m = medium, w = weak, vw = very weak. Relative absorbance at band maximum in parentheses.^c Relative calculated infrared band strength in parentheses.^d Scaled by the factor 0.98.

For ^{19}F NMR, the signals of both molecules are doublets caused by the presence of the P nuclei, which affects the signals splitting them up in two components with coupling constants ($^4J_{\text{FP}}$) of 8 and 10 Hz for $\text{ClF}_2\text{CC}(\text{O})\text{NPCl}_3$ and $\text{CF}_3\text{C}(\text{O})\text{NPCl}_3$, respectively. The shift observed ($\text{CF}_3\text{C}(\text{O})\text{NPCl}_3$, -70.95 ppm and $\text{CF}_2\text{C}(\text{O})\text{NPCl}_3$ -64.2 ppm), is similar to those for HCF_2X ($X = \text{F}, \text{Cl}$) already reported [30].

As it was mentioned, an improvement on the ^{31}P spectra assignment was performed. For instance, it was reported [1] the signals at 3.1 and 3.9 ppm as corresponding to the phosphorous of $\text{CF}_3\text{C}(\text{O})\text{NPCl}_3$ and $\text{CCl}_3\text{C}(\text{O})\text{NPCl}_3$ molecules. However, it is possible to asses that these chemical shifts correspond to the hydrolyzed compounds. Thus, we made a new assignment, and it is shown in Table 5.

Mass spectra

As far as we know, there is no reported data about the mass fragment pattern of the monophosphazenes, i.e. units with one $\text{N}=\text{P}$ group in the backbone, despite of the simplicity of the molecules. Only some results were reported for polyphosphazenes [31,32]. The fragmentation of the title compound shows the most intense peak at $m/z = 178$ corresponding to the loss of a $\cdot\text{CClF}_2$ group, and a signal at $m/z = 85$ due to the same CClF_2^+ fragment. It is worth mentioning that the M^+ ion is not present, as occurs to phosphazenes molecules [1,2].

Vibrational analysis

Assignments reported for related molecules [1,2,4,13,19] were taken into account for the analysis of the current compound, as was quoted in the Introduction section. Although 27 normal modes of vibration are expected for this C_1 symmetry compound, only 21 active modes are observed in the IR and Raman spectra. Table 6 shows a tentative assignment of the fundamental modes and in Fig. 4 are depicted the infrared and Raman spectra for the title compound.

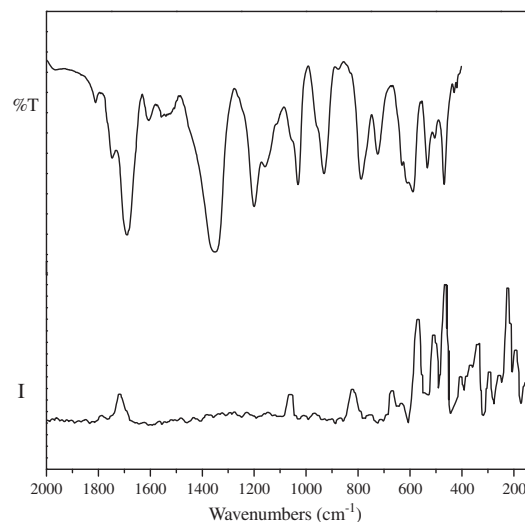


Fig. 4. Infrared (upper trace) and Raman (lower trace) spectra of the liquid $\text{ClF}_2\text{C}(\text{O})\text{N}=\text{PCl}_3$.

$\text{C}=\text{O}$ stretching mode

This normal mode of vibration is assigned to the band located at 1691 and 1695 cm^{-1} in the IR and Raman spectra, respectively. A typical feature in monophosphazenes is the presence of a unique signal in the carbonyl region, as occurs to $\text{CF}_3\text{C}(\text{O})\text{N}=\text{PCl}_3$ and $\text{CCl}_3\text{C}(\text{O})\text{N}=\text{PCl}_3$. In the IR and Raman spectra, there are two signals at higher frequencies (1742 and 1747 cm^{-1} , respectively) which account for the existence of a small amount of $\text{ClF}_2\text{CC}(\text{O})\text{NHP}(\text{O})\text{Cl}_2$ [3], obtained by the $\text{CClF}_2\text{C}(\text{O})\text{NPCl}_3$ hydrolysis with moist air. Considering the $\text{C}=\text{O}$ stretching wavenumbers reported for $\text{CF}_3\text{C}(\text{O})\text{NPCl}_3$ and $\text{CCl}_3\text{C}(\text{O})\text{NPCl}_3$ (1702 cm^{-1} and 1659 cm^{-1} both in IR), it is noticeable the straightforward impact of the electron-withdrawing capacity of the halogens; that is, the larger the electron-withdrawing capacity of the group, the higher

the wavenumber, thus determining the following trend: CCl_3 , CClF_2 and CF_3 .

P=N stretching mode

Monophosphazenes possess a particular vibrational feature, showing a strong band for the P=N stretching mode in the infrared spectra which is not observed in the Raman spectra [33]. In $\text{CF}_3\text{C}(\text{O})\text{N}(\text{PCl}_3)$ and $\text{CCl}_3\text{C}(\text{O})\text{N}(\text{PCl}_3)$ vibrational spectra, this mode is attributed to the signals located at 1389 cm^{-1} and at 1310 cm^{-1} , respectively. Thus, the signal at 1350 cm^{-1} in the IR may be assigned to the P=N stretching mode. This mode is affected by the mesomeric effect, inasmuch as the displacement of the lone pair of the nitrogen atom to the opposite part of the molecule causes a weakening of the P=N bond (see Table 4). Here, the trend CF_3 , CClF_2 and CCl_3 is observed.

C–F stretching modes

Vibrational spectra of molecules containing ClF_2C group have been fully characterized in our research group [3,19,29]. It has been observed that the presence of an atom bulkier than fluorine causes that the vibration of the whole group might be separated in two kinds of vibrations, i.e. C–F and C–Cl. Thus, it is possible to consider the C–F vibration as pure; and consequently, to define two stretching modes (symmetric and antisymmetric). Hence, the CF_2 antisymmetric stretching is attributed to the signals at 1200 cm^{-1} (IR) and 1198 cm^{-1} (Raman), while the corresponding symmetric vibration is assigned to the bands located at 1151 and 1167 cm^{-1} (IR and Raman spectra, respectively). These results are in concordance with the re-assignment reported for CDFA [29] (IR, 1146 cm^{-1}) and for $\text{ClF}_2\text{CC}(\text{O})\text{NHP}(\text{O})\text{Cl}_2$ (1171 cm^{-1}).

C–C stretching mode

This mode is attributed to the bands located at 1030 cm^{-1} (IR) and 1029 cm^{-1} (Raman). These values are in agreement with the reported for $\text{CF}_3\text{C}(\text{O})\text{N}(\text{PCl}_3)$ (1011 cm^{-1} (IR) and 1008 cm^{-1} (Raman)), and for $\text{CCl}_3\text{C}(\text{O})\text{N}(\text{PCl}_3)$ (1055 cm^{-1} (IR) and 1056 cm^{-1} (Raman)). According to the NBO results (Table 4), the $\sigma_{\text{C-X}} \rightarrow \pi_{\text{CO}}^*$ delocalization governs the strength of the C–C bond, because as the delocalization increases, the electron density also increases and thus, the wavenumber shifts towards higher frequencies.

C–Cl stretching mode

The reported wavenumbers of CDFA (970 and 969 cm^{-1} , IR and Raman respectively) and $\text{ClF}_2\text{CC}(\text{O})\text{NHP}(\text{O})\text{Cl}_2$ (976 and 973 cm^{-1} , IR and Raman respectively) led us to assign this mode of vibration to the strong signal at 930 cm^{-1} (IR) and 937 cm^{-1} (Raman).

C–N stretching mode

This mode is assigned to the signals at 787 and 784 cm^{-1} (IR y Raman, respectively). For $\text{CF}_3\text{C}(\text{O})\text{N}(\text{PCl}_3)$ and $\text{CCl}_3\text{C}(\text{O})\text{N}(\text{PCl}_3)$, the same mode is attributed to the bands at 806 cm^{-1} (IR) and 804 cm^{-1} (Raman) for the former, and at 894 cm^{-1} (IR) and 891 cm^{-1} (Raman) for the latter. As can be observed, there is not a clear trend in the frequency positions, that could be due to the absence of the $\text{Lp}_\text{N} \rightarrow \sigma_{\text{CX}}^*$ interaction. This delocalization would reinforce the C–N bond, shifting the signals to higher frequencies (see Table 4).

PCl_3 stretching modes

These modes appear as non-well resolved signals in both infrared and Raman spectra. For a more clear understanding, it is possible to define a local symmetry of the group, where the presence of a plane bisecting the Cl–P–Cl angle, will state symmetric and antisymmetric stretching vibrations with A' and A'' symmetry, assigned to the bands at 612 y 586 cm^{-1} (both into the IR spectra). For $\text{CF}_3\text{C}(\text{O})\text{N}(\text{PCl}_3)$, this mode is located at 612 cm^{-1} (as a shoulder in IR), while the A'' mode is attributed to the 557 cm^{-1} signal in the Raman spectrum. Moreover, the infrared spectra of $\text{CCl}_3\text{C}(\text{O})\text{N}(\text{PCl}_3)$, shows both modes at 618 and a 589 cm^{-1} , respectively. In the $\text{ClSO}_2\text{N}(\text{PCl}_3)$ molecule, these fundamentals are at 630 cm^{-1} (IR) and 599 cm^{-1} (Ra) [13]. The symmetric stretching in $\text{CClF}_2\text{C}(\text{O})\text{N}(\text{PCl}_3)$, is centered at 467 cm^{-1} in both vibrational spectra, while for the perfluoroacetylated compound, the same vibration appears at 494 cm^{-1} in both vibrational spectra as well. For $\text{CCl}_3\text{C}(\text{O})\text{N}(\text{PCl}_3)$, the bands at 494 cm^{-1} and a 497 cm^{-1} in the IR and Raman spectra respectively are assigned to the symmetric vibration.

Conclusions

The novel monophosphazene compound [chloro(difluoro)acetyl]phosphorimidic trichloride ($\text{ClF}_2\text{CC}(\text{O})\text{N}(\text{PCl}_3)$), was prepared and characterized by using GC–MS and multinuclear NMR spectroscopy. The vibrational properties have been investigated by using a combined experimental and theoretical approach. The results are consistent with the presence of a structure with C_1 symmetry in the liquid phase (C=O double bond in *syn* position with respect to the P=N double bond). The calculated wavenumbers were fitted according to the Wavenumber–Linear–Scaling Method, obtaining improvements in the simulated spectra, despite the reported statements that the method is not appropriate for halogenated compounds.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.saa.2013.09.113>.

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