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UV photoelectron and ab initio study of intramolecular interactions in α-diethoxyphosphoryl carbonyl derivatives

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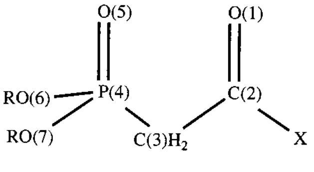
Abstract

Information on the geometric and electronic structures of α-diethoxyphosphoryl carbonyl derivatives, $(RO)_2P(O)CH_2C(O)X$, (**1**–**5**, $X = CH_3$ **1**, CH_3CH_2O **2**, CH_3CH_2S **3**, C_6H_5 **4**, $(CH_3CH_2)_2N$ **5**), is obtained by UV photoelectron spectroscopy and ab initio calculations. At the HF level, the CH_2–P bond is *gauche* to the carbonyl group except in **5**. However, at the DFT and MP2 levels, the *gauche* conformation prevails for all the derivatives, in agreement with the spectroscopic data. This conformation is dictated by the interplay of the electronic interactions between the XC(O) and $(RO)_2P(O)$ groups with two short contacts between pairs of oppositely charged atoms. The negatively charged carbonyl oxygen and one of the oxygen atoms bonded to phosphorus lie at distances shorter than (or close to) the sum of the corresponding van der Waals radii from the positively charged phosphorus and carbonyl carbon atom, respectively. The presence of through-space interactions in the ground and ionised states is confirmed by eigenvector analysis and by the shifts in the MO energies with respect to those of reference compounds. In the ground state the non-bonded interactions are weaker than the corresponding interactions in β-carbonyl sulphones, $RSO_2CH_2C(O)X$, because of the less suitable geometry of the PO_3 group, with respect to the SO_2R group, for interaction with the β-carbonyl group. In the ionised state, however, the negative charge on the oxygens of the phosphoryl group has a greater capacity to relax toward the ionised XC(O) group thus reducing the ionisation energy values. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Photoelectron spectroscopy; Conformational analysis; Ab initio calculations; Electronic structures

1. Introduction

Over the last few years we have investigated the interplay between the geometric and electronic structures of β-thio carbonyl derivatives, $RC(O)CH_2X$ (R = alkyl, aryl and heteroatom-containing group; X = SR, S(O)R and $S(O)_2R$) in the gas and condensed phases. The results of X-ray diffraction, ultraviolet photoelectron (UP), electron transmission (ET), IR and ^{13}C-NMR spectroscopy together with the results of ab initio calculations indicate that β-carbonyl-sulphides and -sulphones prefer a conformation in which the CH_2–S bond is *gauche* to the carbonyl group [1–3], the stabilisation deriving in part from hyperconjugative interaction between the two groups. An interesting observation regarding β-carbonyl sulphones is that the O/CO···S and, particularly, the O/SO_2···C/CO contacts



$X = CH_3$ **1**, CH_3CH_2O **2**, CH_3CH_2S **3**, C_6H_5 **4**, $(CH_3CH_2)_2N$ **5**

α = O(1)-C(2)-C(3)-P(4)
β = C(2)-C(3)-P(4)-O(5)
γ = C(2)-C(3)-P(4)-O(6)
γ ' = C(2)-C(3)-P(4)-O(7)

Scheme 1.

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are shorter than the sum of the corresponding van der Waals radii [4] and that these contacts occur between pairs of oppositely charged atoms. Through-space and through-bond mixing [5] between the carbonyl and sulphonyl groups is confirmed by eigenvector analysis and orbital energy shifts with respect to reference compounds.

In contrast, in α-sulphinyl acetophenones, PhC(O)-$CH_2S(O)R$ (R = alkyl and phenyl), the CH_2–S bond is *quasi cis* to the carbonyl group [6,7]. The *cis* conformer of sulphoxides is stabilised by a strong non-bonded interaction between the negatively charged carbonyl oxygen and the positively charged sulphur atom from which it is separated by a distance (2.8–2.9 Å) much shorter than the sum of the van der Waals radii. The predominant charge transfer interaction (O/CO → S), therefore, occurs in the opposite direction than in related sulphones ($O/SO_2 \rightarrow C/CO$). The inversion of the charge transfer direction (and the change of the *cis*-*gauche* orientation of the thio group) from sulphone to sulphoxide is associated with an increase of electron affinity of the thio group in the latter, and could explain its smaller thermal stability [6]. Therefore, electronic interactions dominate the preference for the most stable conformation. Steric hindrance exerts only a secondary influence which might prevail in the presence of a bulky substituent. $PhC(O)CH_2S(O)Bu^t$, in fact, has a *cis* conformation in the solid phase, but a *gauche* one in both liquid (IR data) and gas (HF/6-31G**) phases [7].

In this context, we present here the results of a UP spectroscopic and theoretical (HF, DFT and MP2) study of the electronic and geometric structure of some α-diethoxyphosphoryl carbonyl derivatives, $(EtO)_2P(O)CH_2C(O)X$ listed in Scheme 1, in order to elucidate the conformation and the dominant electronic interactions. Preliminary results obtained from IR and ^{13}C-NMR spectroscopy indicate [8] that, in solution, these compounds possess only one, *gauche*, conformer whose O/PO → C/CO charge transfer interaction is weaker than the $O/SO_2 \rightarrow C/CO$ one in the corresponding sulphones.

2. Experimental

2.1. UP spectra

The HeI UP spectra were recorded on a Perkin–Elmer PS 18 photoelectron spectrometer connected to a Datalab DL4000 signal analysis system. The UP spectra are of low intensity and poor resolution probably because of partial decomposition in the inlet system and/or in the ionisation chamber of the spectrometer. However, samples of each compound were loaded into the UPS inlet system at least twice, and a minimum of three reproducible UP spectra were obtained during each run. The UP bands were located using the positions of their maxima, which were taken as corresponding to the vertical ionisation energy (IE) values and calibrated against rare gas lines. The accuracy of the IE values was estimated to be ± 0.05 eV (± 0.1 eV for shoulders). The assignment of the UP spectra is based upon those of simple related molecules. Diethyl ethylphosphonate, $(EtO)_2P(O)Et$ (**6**), was taken as the reference compound for the phosphoryl group IE values, and the compounds of general formula $CH_3C(O)X$ [2] and $CH_3SO_2CH_2C(O)X$ (X = CH_3, EtO, EtS, Et_2N [3]) and acetophenone, **4a** [9], were taken as reference compounds for the carbonyl lone pair (n_{CO}) and the π_{ring} or π_X (where X contains a heteroatom) IE values. The assignment of the UP spectra was assisted by the analysis of the relative intensity of the π_X and n_{CO} and phosphoryl bands in the present derivatives and with respect to the reference compounds.

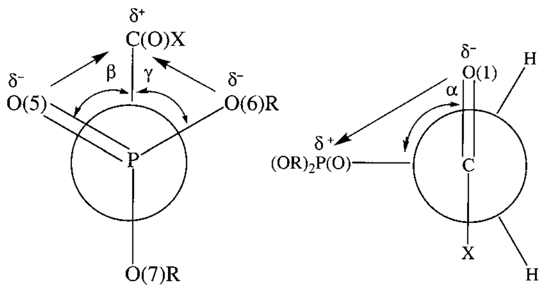
2.2. Calculations

The energy and the localisation properties of the relevant molecular orbitals (MOs), the electron charge distribution at the various atoms and/or groups, and the geometric parameters were computed at the ab initio 6-31G** level using the Gaussian 98 program [10]. The starting conformations had the phosphorus atom in a *cis* or *gauche* orientation with respect to the carbonyl group and the angle between the C(2)–C(3) and P(4)–O(5) bonds ranging from 40 to 180°. To save computer time, the ethyl groups were replaced with methyl groups. All the parameters were allowed to vary independently in the optimisation procedure. The two most stable conformations of **1**–**5** were then optimised at the DFT (B3LYP) [11] level and those of **1** and **5** also at the MP2 (frozen-core) level, always using the same 6-31G** basis and allowing complete relaxation. The geometry of the reference compounds **6**, **4a** and α-methylsulphonylpropanone, $CH_3SO_2CH_2C(O)CH_3$ (**7**), was optimised at the HF/6-31G** level.

3. Results and discussion

3.1. Geometric structure and charge distribution

The dihedral angles α = O(1)–C(2)–C(3)–P(4), β = C(2)–C(3)–P(4)–O(5), γ = C(2)–C(3)–P(4)–O(6) and γ' = C(2)–C(3)–P(4)–O(7) (see Scheme 2) for the most stable conformers of compounds **1**–**5** computed at the HF and DFT levels, and also at the MP2 level for **1** and **5,** are listed in Table 1. The O(1)–C(2), P(4)–O(5) and P(4)–C(3) bond lengths and the interatomic distances O(1)···P(4), O(5)···C(2), and O(6)···C(2) (where O(6) is the O/OR atom closest to the carbonyl carbon



Scheme 2.

C(2)) are listed in Table 2 together with the corresponding bond lengths for the reference compounds **6** and **4a** and the relevant sums of the van der Waals radii [4]. The Mulliken charges at selected atoms for compounds **1**–**6** and **4a** are presented in Table 3.

At the HF level, compounds **1**–**4** prefer a conformation in which the C(3)–P(4) bond is *gauche* or *quasi gauche* to the carbonyl group (44.9° ≤ α ≤ 84.4°), while **5** prefers a *cis* orientation ($\alpha = 17.6°$), the energy of the *gauche* rotamer being some 2.5 kJ mol^{-1} higher. This result contrasts with the analysis of the IR and ^{13}C-NMR spectra [8] which indicates the presence of only one, *gauche*, conformer along the series. DFT calculations, however, reverse the energy ordering of the two most stable conformers of **5**, leaving unchanged the conformer ordering for the remaining derivatives, so that a *gauche* rotamer (50.1° ≤ α ≤ 96.9°) is predicted to be the most stable for **1**–**5**. The results of the DFT calculations for **1** and **5** are fully confirmed at the MP2 level (see Table 1). The *gauche* conformer of **5** is 3.73 and 6.18 kJ mol^{-1} more stable than the *cis* one at the DFT and MP2 level, respectively. The second minimum for **1**–**4** also has a *gauche* conformation, its HF energy being 2.9–7.7 kJ mol^{-1} higher than that of the absolute minimum (see Table 1). Analysis of the vibrational frequencies to check the stability of the optimised struc-

Table 1

Computed values of the dihedral angles (°) α = O(1)–C(2)–C(3)–P(4), β = C(2)–C(3)–P(4)–O(5), γ = C(2)–C(3)–P(4)–O(6) and γ' = C(2)–C(3)–P(4)–O(7) for the most stable, *gauche*, conformer of α-dimethoxyphosphoryl carbonyl derivatives, $(MeO)_2P(O)CH_2C(O)X$, and the energy differences (ΔE, kJ mol^{-1}) between the absolute minimum and the second lowest one

	X	Theory level [a]	α	β	γ	γ'	ΔE
1	CH_3	HF	82.2	45.6	−81.8	171.6	4.78
		DFT	87.2	45.6	−82.9	172.3	2.75
		MP2	84.7	44.2	−83.8	171.5	1.25
2	CH_3O	HF	56.0	50.0	−78.6	175.3	7.67
		DFT	57.0	50.7	−78.8	176.9	7.84
3	CH_3S	HF	44.9	52.9	−76.1	177.8	5.04
		DFT	50.1	52.2	−77.7	178.1	2.89
4	C_6H_5	HF	84.4	57.9	−70.2	−176.6	2.88
		DFT	90.5	63.7	−65.5	−170.1	1.39
5	$(CH_3)_2N$	HF [b]	17.6	64.3	−67.3	−172.5	−2.54
		HF	94.1	77.1	−49.0	−159.1	0.0
		DFT	96.9	78.7	−46.9	−157.0	3.73
		MP2	98.6	78.9	−46.7	−156.2	6.18

[a] 6-31G** basis set.

[b] The *cis* conformer, the most stable one at the HF level.

Table 2

Selected bond distances and short interatomic distances and sums of the van der Waals radii (vdW, Å) computed at the HF/6-31G** level for the *gauche* conformer of α-dimethoxyphosphoryl carbonyls, $(MeO)_2P(O)CH_2C(O)X$ and the reference compounds dimethyl methylphosphonate and acetophenone

	X	O(1)···P(4)	O(5)···C(2)	O(6)···C(2) [a]	$d_{O(1)–C(2)}$	$d_{P(4)–C(3)}$	$d_{P(4)–O(1)}$
1	CH_3	3.331	3.128	3.416	1.193	1.810	1.459
2	CH_3O	3.169	3.200	3.391	1.190	1.812	1.456
3	CH_3S	3.101	3.257	3.387	1.189	1.814	1.456
4	C_6H_5	3.394	3.306	3.341	1.197	1.809	1.458
5	$(CH_3)_2N$	3.494	3.502	3.159	1.207	1.813	1.455
6	$(MeO)_2P(O)Me$					1.790	1.459
4a	Acetophenone				1.196		
	vdW [b]	3.32	3.22				

[a] O(6) is the O/OR atom closer to the carbonyl carbon atom (C(2))

[b] Sums of the van der Waals radii from Ref. [5].

Table 3
Charges at selected atoms (e) computed at the HF/6-31G** level[a] for the *gauche* conformer of α-dimethoxyphosphoryl carbonyls, $(MeO)_2P(O)CH_2C(O)X$ and the reference compounds dimethyl methylphosphonate and acetophenone (a minus sign indicates an excess of negative charge)

	X	O(1)	C(2)	P(4)	O(5)	O(6) [b]	O(7)
1	CH_3	−0.523	0.498	1.577	−0.740	−0.718	−0.700
2	CH_3O	−0.572	0.782	1.571	−0.726	−0.721	−0.703
3	CH_3S	−0.516	0.339	1.579	−0.723	−0.721	−0.705
4	C_6H_5	−0.541	0.514	1.576	−0.738	−0.716	−0.701
5	$(CH_3)_2N$	−0.629	0.763	1.612	−0.718	−0.702	−0.738
6	(MeO)2P(O)Me			1.554	−0.743	−0.713	−0.713
4a	Acetophenone	−0.540	0.538				

[a] 6-31G** basis set.

[b] O(6) is the O/OR atom closer to the carbonyl carbon atom (C(2)).

tures was not performed because the same energy minima were obtained using different starting geometries and different theoretical methods.

Bond distances and bond angles in the $(RO)_2P(O)$-CH_2– fragment are almost independent of the X substituent and close to the corresponding values for reference compound **6**. In particular, the P=O bond distance is independent of X, while, the carbonyl O(1)–C(2) bond length varies with X as previously observed [2,3] for the $XC(O)SO_2R$ and $XC(O)CH_3$ derivatives corresponding to **1**–**5** showing the expected [12] elongation on going from esters to ketones, to amides (see Table 2).

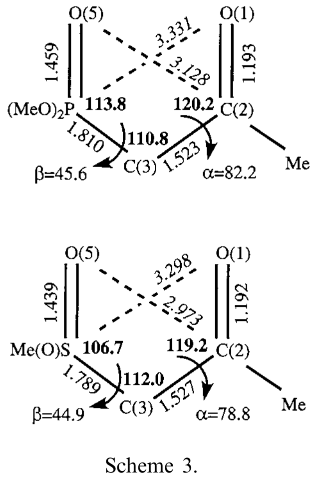
The phosphorus atom bears a high positive charge (ca. 1.6 e), while a negative charge (0.70 to 0.74 e) is present on the oxygen atoms, the apical oxygen bearing the highest (see Table 3). The charge at the two O/OR atoms of **6** is equal for symmetry reasons, but in **1**–**5** it increases at O(6) with respect to O(7) disclosing the presence of an electrostatic interaction with the oppositely charged C(2) atom in agreement with the indications from vibrational spectra [8]. The $(RO)_2P(O)$ group in **6** bears a negative charge (0.130 e). The charge is positive and nearly constant (0.198–0.212 e) in **1**–**5** because of the nearly constant electron withdrawing inductive effect of the C(O)X substituent [13,14].

The O(1)···P(4), O(5)···C(2) and O(6)···C(2) interatomic distances are close (± 0.2 Å) to the corresponding sums of their van der Waals radii (see Table 2 and Scheme 2). They are linearly related to the relevant dihedral angles α, β and γ (see Scheme 2). Small α values in **2** and **3** are associated with O(1)···P(4) contacts shorter than the sum of their van der Waals radii. The corresponding interaction prevails in α-sulphinyl acetophenones which prefer *cis* conformations [6,7]. Large α values in **1** and **5** are associated with short O(5)···C(2) or O(6)···C(2) contacts, as found for the corresponding contacts in sulphones which prefer a *gauche* conformation [1,3]. Compound **4** follows a different trend because of the high steric hindrance of the phenyl substituent. In both cases the contacts between the oppositely charged atoms are longer (>3.1 Å) than the relevant contacts in the thio-derivatives (<3.0 Å).

To compare the geometric factors determining the interaction between pairs of oppositely charged atoms, the relevant portions of the molecular skeletons of **1** and **7** are shown, as examples, in Scheme 3. At the HF/6-31G** level, the S–C(3) (1.789 Å) and S=O (1.439 Å) bond distances and the C(3)–S–O(5) (106.7°) bond angle in **7** are smaller than the corresponding P–C(3) (1.810 Å), P=O (1.459 Å) and C(3)–P–O(5) (113.8°) values in **1**. This allows the α (82.2° (**1**) and 78.8° (**7**)) and β (45.6° (**1**) and 44.9° (**7**)) dihedral angles to assume slightly smaller values in the sulphonyl derivatives which, in turn, leads to shorter contacts as shown in Scheme 3. Smaller ground state interactions between the phosphoryl and carbonyl groups than between the thio and carbonyl groups have been proposed to rationalise the IR and ^{13}C-NMR spectra [8].

3.2. UP spectra

The UP spectra of compounds **1**–**6** are presented in Fig. 1. Table 4 lists the low IE values thereof obtained



Scheme 3.

together with the relevant values for the reference compounds $XC(O)CH_3$ (**1a**–**5a**) [2,9], and $XC(O)CH_2SO_2CH_3$ (**1b**–**5b**) [3], X = CH_3, CH_3CH_2O, CH_3CH_2S, C_6H_5, $(CH_3CH_2)_2N$.

The low IE region of the UP spectrum of **6** shows three partially resolved bands peaking at 10.30, 10.75 and 11.30 eV. The corresponding bands (10.71, 11.26 and 11.83 eV) in the spectrum of dimethyl methylphosphonate, $(CH_3O)_2P(O)CH_3$, have been ascribed [15] to MOs mainly localised at the oxygen atoms. This assignment is in agreement with the results of the calculations and with other experimental data indicating [16,17] that ionisation from MOs mainly localised at the P–C, C–C and C–H bonds occurs at higher energy than from oxygen lone pair orbitals. In particular, the calculations predict that the three outermost MOs of **6** derive from the 2p AOs of the apical oxygen lying in the *x*,*y* plane perpendicular to the P=O bond. The first MO, mainly p_x, is destabilised by interaction with the orbital localised at the P–C bond, the second and the third one derive from the combination of p_y with the out-of-phase combinations of the p_z and the p_y plus p_x orbitals, respectively, of O(6) and O(7).

The poor quality of some of the spectra does not allow detailed speculations. However, a comparison of peak shape and relative intensity and of the IE values obtained from the spectra of **1**–**5** with the relevant data for the reference compounds indicates that IE values ≤ 9.7 eV can be related to ionisation from the π_x (or the two uppermost π_{ring}) and n_{CO} orbitals, while IE values between 10.2 and 11.5 eV (except in **2**) can be related to $(EtO)_2P(O)$ ionisation processes. The HF calculations reproduce the main experimental IE trends

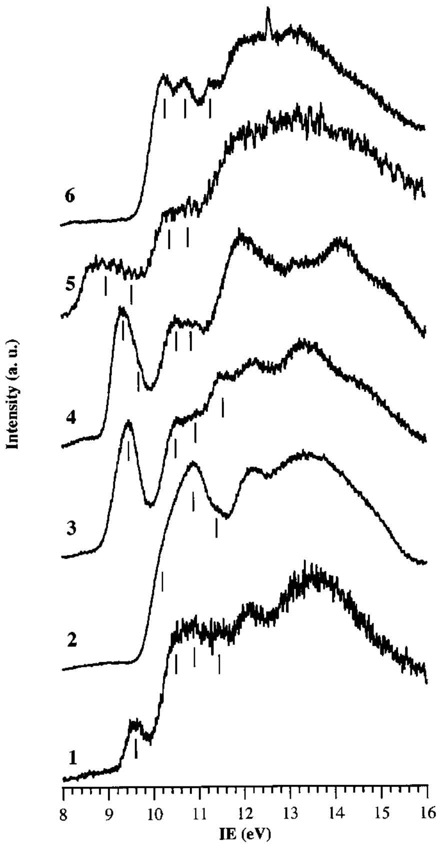


Fig. 1. HeI UP spectra of α-diethoxyphosphoryl carbonyl derivatives, $(RO)_2P(O)CH_2C(O)X$, (**1**–**5**, X = CH_3 **1**, CH_3CH_2O **2**, CH_3CH_2S **3**, C_6H_5 **4**, $(CH_3CH_2)_2N$ **5**), and $(EtO)_2P(O)Et$ (**6**).

Table 4
Ionisation energy values (eV) of compounds **1**–**6** and of the reference compounds $XC(O)CH_2Y$, Y = H, **1a**–**5a** and Y = SO_2CH_3, **1b**–**5b**

	X	Y	π_X or π_{ring}	n_{CO}	$(EtO)_2P(O)$ or SO_2 orbitals			
1	Me	$Et_2P(O)$		9.60	10.50	10.90	11.45	
2 [a]	EtO	$Et_2P(O)$		(10.2_{sh})		10.89	(11.4_{sh})	
3	EtS	$Et_2P(O)$	9.47	9.47	10.50	10.95	11.55	
4	C_6H_5	$Et_2P(O)$	9.36, 9.7_{sh}	9.36	10.53	10.85		
5	Et_2N	$Et_2P(O)$	8.98	9.55	10.39	10.80		
6	Diethyl ethylphosphonate				10.30	10.75	11.30	
1a [b]	Et	H		9.46				
2a [b]	EtO	H	10.98	10.45				
3a [b]	EtS	H	9.4_{sh}	9.65				
4a [c]	C_6H_5	H	9.38, 9.8_{sh}	9.57				
5a [b]	Et_2N	H	8.71	9.20				
1b [d]	Me	SO_2Me		10.10	10.81	11.31	11.75_{sh}	12.06
2b [d]	EtO	SO_2Me	11.30	10.65	10.95_{sh}	11.55_{sh}	11.85	12.20
3b [d]	EtS	SO_2Me	9.65	9.93	10.75	11.25	11.65_{sh}	12.02
4b [d]	C_6H_5	SO_2Me	9.71	9.71	10.55	11.15	11.7_{sh}	12.1
5b [d]	Et_2N	SO_2Me	9.13	9.60	10.60	11.05	11.65	12.07

[a] In the energy region of interest the spectrum shows only one intense band peaking at 10.89 eV with shoulders at about 10.2 and 11.4 eV (see Fig. 1).

[b] From Ref. [2].

[c] From Ref. [9].

[d] From Ref. [3].

along the series and on going from the reference compounds to the studied derivatives. In particular, the computed IE_1 and IE_2 values for the *gauche* conformer of **5** are 0.2 eV closer, in Koopmans' approximation, to the experimental data than those computed for the *cis* rotamer. In addition, the experimental IE_3–IE_2 splitting (0.84 eV) is better reproduced by the calculations for the *gauche* rotamer (0.71 eV) than for the *cis* one (0.21 eV). The prevalence of the *gauche* conformation for **5** indicated by the DFT and MP2 calculations is, thus, confirmed. Inspection of Table 4 shows that for **2**, the ionisation values from the two fragments XC(O) and $(EtO)_2P(O)$ overlap. In fact, the spectrum of **2** presents only one intense band peaking at 10.89 eV with shoulders at 10.2 and 11.4 eV. These IE values have a wider spread than the values of the reference compounds indicating interaction between the orbitals of the two fragments.

Ionisation from the XC(O) fragment, namely π_x or π_{ring} (ΔIE 0.1–0.2 eV) and mainly n_{CO} ($\Delta IE \leq 0.5$ eV, except in **5**) occurs at lower energy than in the corresponding β-carbonylsulphones [3], despite the Swain–Lupton electron-withdrawing field-inductive parameters of the $(EtO)_2P(O)$ and SO_2Et groups being quite close to each other ($I = +0.52$) [18]. Furthermore, the n_{CO} IE value in **1**–**4** is lower than or similar to that in the XC(O)Me series [2] which lacks the electron-withdrawing substituent, while only in **5** is it significantly higher ($\Delta IE = 0.35$ eV) than in the corresponding **5a** (see, however, below). A possible explanation of these findings is provided by eigenvector analysis which discloses the presence of through-space mixing [5] between the n_{CO} orbital and the lower lying oxygen AOs of the PO_3 group. An additional explanation, more important when the comparison is made between SO_2Et and $(EtO)_2PO$ derivatives, resides in the conformation and electronic structure of the phosphoryl derivatives. Scheme 2 shows that the positively charged C/CO atom lies between and close to two (O(5) and O(6)) negatively charged oxygen atoms. The sum of these C···O distances (6.54–6.66 Å) is only slightly larger than twice the sum of the relative van der Waals radii (6.44 Å). Thus, the $(RO)_2P(O)$ group has two O atoms close enough for CT electronic relaxation upon XC(O) ionisation, both carrying a higher negative charge (0.72 ± 0.02 e) compared to the single interacting O atom in the SO_2R group which also carries a lower negative charge ($q_O = 0.68 \pm 0.01$ e) [3]. Therefore, the electronic relaxation toward the ionised XC(O) fragment is larger from the more polarisable phosphoryl group than from the sulphonyl group, reducing the measured IE values. The higher relaxation from the PO_3 than from the SO_2 group is in line with the higher basicity of the oxygen atom of diethyl ethylphosphonate [19] than dimethylsulphone [20] with respect to phenol. In fact, the variations in the IE values of the lone pair electrons reflect the abilities of the substances to donate their electrons, and the IE values are related to the gas phase basicity [21]. The amino derivative, **5**, somewhat deviates from this behaviour because the n_{CO} and π_x IE values are close to the corresponding values for **5b**. This is likely due to the presence of additional intramolecular interactions between the oxygen atoms and the positively charged hydrogens of the amino group.

The PO_3 group IE values are higher than the corresponding values of reference compound **6**. This stabilisation is a ground state effect because it is reproduced by the computed energy levels and can, in part, be ascribed to the inductive effect of the XC(O) groups ($I_{XC(O)}$ ca. -0.30) [13]. However, eigenvector analysis unveils the presence of mixing of the PO_3 orbitals with the carbonyl oxygen AOs. The stabilisation does not manifest itself in the spectrum of **5** probably because of a compensating effect with relaxation from O(1) which bears by far the highest negative charge (see Table 3) and possesses the highest HOMO energy (see Table 4).

4. Conclusions

In agreement with the analysis of the IR spectra[8], the DFT calculations indicate that the C(3)–P bond of α-diethoxyphosphoryl carbonyls, $(RO)_2P(O)CH_2C(O)X$, prefers a *gauche* conformation with respect to the carbonyl group. This conformation is stabilised by orbital mixing and electrostatic interactions between oppositely charged atoms of the CO and PO_3 groups. In particular, when O(1)···P is the shortest non-bonded interaction, as in **2** and **3**, the α dihedral angle assumes a small value (50–57°) resembling the *quasi cis* conformation of β-carbonyl sulphoxides [6,7]. However, when the short contact occurs between O(5) or O(6) and C(2), α assumes large values (87–97°), as in **1** and **5**, resembling the *gauche* conformation of the corresponding sulphones [1–3]. In both cases, however, the contacts are close to the sum of the van der Waals radii (3.2–3.3 Å) and, therefore, the ground state interactions between the CO and PO_3 groups are smaller than the CO/SO_n ones of the corresponding thio-derivatives (where the contacts are shorter than 3.0 Å), in agreement with the analysis of the ^{13}C-NMR spectra.

UP spectral features show, by comparison with reference compounds, that the lowermost IE values (≤ 9.7 eV) are related to ionisation from the XC(O) group. The π_x (or π_{ring}) and n_{CO} ionisation values are close to the corresponding data from **1a**–**5a** which lack the electron-withdrawing group, and much lower than the corresponding data from sulphones **1b**–**5b**, despite the equal inductive effects of the SO_2 and $(RO)_2P(O)$ groups. This IE reduction in part derives from CO/PO_3 group orbital interaction and in part is a final state effect. In fact, owing to the propitious conformation (see Scheme 3), the negative charges of two O/PO_3 atoms can relax toward the ionised XC(O) group instead of the charge of a single oxygen atom in the corresponding sulphones. In addition, the phosphoryl group is more polarisable than the sulphonyl group because the P–O bonds are longer than the S–O ones and the partial negative charges at O/PO_3 are larger than at O/SO_2.

The presence of the electronegative XC(O) group increases the IE values from the PO_3 group with respect to **6**. In addition, the above cited CO/PO_3 orbital mixing contributes to the observed IE increase. Only **5** shows a final state effect due to the presence of a large and highly polarisable (low π_x IE value) negative charge at O/CO.

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