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Stereochemical and electronic interaction studies of some *meta*- and *para*-substituted α-methylsulfinyl-α-diethoxyphosphorylacetophenones

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Abstract

The IR and ^{1}H NMR spectra analyses of some *meta*- (Y=OMe **1**, Me **2**, F **3**, Cl **4**, Br **5** and NO$_2$ **6**) and *para*- (Y=OMe **7**, H **8**, F **9**, Cl **10**, Br **11** and NO$_2$ **12**) substituted α-methylsulfinyl-α-diethoxyphosphorylacetophenones m,p-YPhC(O)C*H[S*(O)Me][P(O)(OEt)$_2$], along with theoretical calculations at the B3LYP/6-31 + g(d,p) level, for compound **8**, have shown, in solution of solvents of increasing polarity and in the gas phase, the existence of two enantiomeric pairs (racemic mixtures). The more stable and less polar (C$_S$S$_S$; C$_R$S$_R$) enantiomeric pair (conformer pair **I**) display the [MeS(O)] group in a *quasi-periplanar* (*quasi-cis*) geometry and the [P(O)(OEt)$_2$] group in a *anti-clinal* (*gauche*) geometry relative to the carbonyl group. The less stable and more polar (C$_R$S$_S$; C$_S$S$_R$) enantiomeric pair (conformer pair **II**) presents both substituents in a *syn-clinal* (*gauche*) geometry. The observed solvent effect on the IR ν_{CO} doublet components and on the two ^{1}H NMR methyl signals relative intensities, for the whole series along with the complete deuterium exchange of the α-methine hydrogen atom of **1**, strongly indicate that both pairs of diastereomers [(C$_S$S$_S$; C$_R$S$_R$) and (C$_R$S$_S$; C$_S$S$_R$)] are equilibrated in solution through an intermediate enolic form. The more stable (C$_S$S$_S$; C$_R$S$_R$) enantiomeric pair [conformer pair (**I**)] is strongly stabilised by O$_{(CO)}^{\delta-}$···S$_{(SO)}^{\delta+}$ charge transfer and electrostatic interaction, while the remaining electronic interactions are almost counterbalanced among themselves, and are important in the stabilisation of the less stable (C$_R$S$_S$; C$_S$S$_R$) enantiomeric pair [conformer pair (**II**)]. Compound **1**, in the solid state, occurs as the (C$_R$S$_S$; C$_S$S$_R$) enantiomeric pair [conformer pair (**II**′)], as determined by X-ray diffraction analysis, whose geometry is similar to conformer pair (**II**), found in gas phase. The O$_{(CO)}^{\delta-}$···S$_{(SO)}^{\delta+}$, O$_{(POEt)}^{\delta-}$···C$_{(CO)}^{\delta+}$, O$_{(POEt)}^{\delta-}$···S$_{(SO)}^{\delta+}$ and H$_{(o-Ph)}^{\delta+}$···O$_{(CO)}^{\delta-}$ intramolecular interactions contribute for the stabilisation of conformer pair (**II**′) in the solid. Further stabilisation derives from dipole moment couplings and by an intricate network of electrostatic interactions (hydrogen bonds).
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1. Introduction

Our previous spectroscopic (IR, ^{13}C NMR, UV and UPS), X-ray diffraction and theoretical studies on some

β-carbonyl-sulfoxides, X-C(O)CH$_2$S(O)R (X=Me, Ar, NR$_2$, OR and SR; R=Me, Ar) [1–5], have shown that their *gauche* conformer is the most stable, but the *cis* conformer prevails for the α-sulfinylacetophenones, X-C(O)CH$_2$S(O)R [X=Ph; R=Me, Et, [i]Pr and Ph] [6,7] and [X=p-Y-Ph (for Y=OMe, Me, H, Cl, and Br; R=Et)] [8], except for R=[t]Bu for the former series, and (Y=CN and NO$_2$; R=Et) for the latter one. The stabilisation of

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the *gauche* conformers has been ascribed to the π_{CO}/σ^*_{C-S} and, to a minor extent, to the π^*_{CO}/σ_{C-S} orbital interactions, while the stabilisation of the *cis* conformers was attributed to the electrostatic interaction between the C=O and S=O dipoles, along with the $\pi^*_{SO}-n_{O(CO)}$ charge transfer (CT) interaction. Furthermore, our spectroscopic (IR, ^{13}C NMR and UPS) and theoretical (HF, DFT and MP2) studies of some β-carbonyl-phosphonates X-C(O)CH₂P(O)(OEt)₂ [X=Me, *p*-Y-Ph (Y=OMe, Me, H, Cl, Br, CN, NO₂), NR₂, OR and SR] [9–11] have shown, that these compounds occur as a single *gauche* conformer, being its stabilization attributed to the crossed $O^{\delta-}_{(PO)}\cdots C^{\delta+}_{(CO)}$ (stronger) and $O^{\delta-}_{(CO)}\cdots P^{\delta+}_{(PO)}$ electrostatic and CT interactions.

In order to investigate which are the electronic interactions, that stabilise the preferred conformations when the acetophenone moiety has in the α position, both the [S(O)R] and [P(O)(OEt)₂] substituents, the present paper reports the IR and NMR spectrocopic and density functional theory (DFT) studies of some *meta*- (Y=OMe **1**, Me **2**, F **3**, Cl **4**, Br **5** and NO₂ **6**) and *para*- (Y=OMe **7**, H **8**, F **9**, Cl **10**, Br **11** and NO₂ **12**) substituted α-methylsulfinyl-α-diethoxyphosphorylacetophenones (Scheme 1), along with the X-ray diffraction analysis of compound **1**. These compounds were chosen, taking into account that the orbital and Coulombic interactions which could act in their conformers, should be directly affected by changes of the inductive and conjugative effects involving the *meta* and *para* substituents at the phenacyl group, and, consequently, should influence the stabilization of the presented conformers.
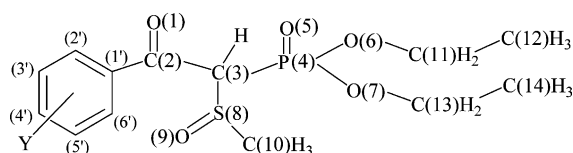
Y$_{meta}$ = OMe **1**, Me **2**, F **3**, Cl **4**, Br **5**, NO₂ **6**

Y$_{para}$ = OMe **7**, H **8**, F **9**, Cl **10**, Br **11**, NO₂ **12**

α = O(1)-C(2)-C(3)-P(4)

α' = O(1)-C(2)-C(3)-S(8)

β = C(2)-C(3)-P(4)-O(5)

β' = C(2)-C(3)-S(8)-O(9)

γ = C(2)-C(3)-P(4)-O(6)

γ' = C(2)-C(3)-P(4)-O(7)

γ'' = C(2)-C(3)-S(8)-C(10)

δ = C(3)-P(4)-O(6)-C(11)

δ' = C(3)-P(4)-O(7)-C(13)

ϕ = O(1)-C(2)-C(1')-C(2')

ω = C(6')-C(5')-O-CH₃

Scheme 1.

2. Experimental

2.1. Materials

All solvents for IR measurements were spectrograde and were used without further purification. The *m*- and *p*-substituted acetophenones (**13–24**) were commercially available, while *m*- (**1–6**) and *p*-substituted α-methyl-sulfinyl-α-diethoxyphosphorylacetophenones (**7–12**) were prepared as previously described [12,13]. *m*-Methoxy-α-deutero-α-methylsulfinyl-α-diethoxyphosphorylaceto-phenone was prepared by the reaction of a compound **1** (0.06 mmol), in 0.5 ml of deuterochloroform solution, stirred with 0.5 ml deuterium oxide during 12 h, at room temperature. After usual work up the obtained product showed, through its ^{1}H NMR spectrum, in CDCl₃, more than 95% of deuterium exchange.

2.2. IR measurements

The IR spectra were obtained on a FT-IR Nicolet Magna 550 spectrometer, with 1.0 cm⁻¹ resolution. The carbonyl region (1800–1600 cm⁻¹) was recorded for carbon tetra-chloride, chloroform and acetonitrile solutions, at a concentration of 2.0×10^{-2} mol/dm³, using a 0.519 mm sodium chloride cell. The carbonyl first overtone region (3600–3100 cm⁻¹) was recorded for a carbon tetrachloride solution (2.0×10^{-2} mol/dm³) using a 1.00 cm quartz cell. The overlapped carbonyl bands (fundamental and first overtone) were deconvoluted by means of the Grams/32 curve fitting program, version 4.04 Level II [14]. The relative concentrations of the **I** (C$_S$S$_S$; C$_R$S$_R$) and **II** (C$_R$S$_S$; C$_S$S$_R$) conformers were estimated from the absorbance ratio α_I/α_{II}, at the maxima of the carbonyl band components, assuming as an approximation equal absorptivities for the two conformers.

2.3. NMR measurements

^{1}H NMR spectra were recorded on a Varian Inova 1 spectrometer operating at 299.947 MHz, for 0.1 mol/dm³ solutions, in carbon tetrachloride, chloroform-*d* and aceto-nitrile-*d₃*. [1]H chemical shifts are reported in ppm relative to TMS, as internal standard.

2.4. X-ray measurements

Crystal data: C₁₄H₂₁O₆PS, $M=348.34$, monoclinic, P2₁/c, $a=8.1883(9)$, $b=9.0738(8)$, $c=23.219(2)$ Å, $\beta=95.311(4)°$; $V=1717.8(3)$ Å³, $Z=4$, $D_x=1.347$ mg/m³, λ (Mo Kα)$=0.71073$ Å, $R_1=0.0461$.

2.5. Data collection and processing

X-ray diffraction data were collected on a CAD4 diffractometer with the ω/2θ scan technique, graphite

monochromated Mo Kα radiation, $T = 293$ K. Full matrix least-squares refinement on $F^2 = 5310$ Reflections were collected up to $2\theta_{max} = 60°$. During data collection, the intensity of three standard reflections were monitored every 30 min of X-ray exposure time, showing no significant decay. Data were corrected for Lorentz-polarization effects. H-atoms were located on stereochemical grounds and refined with fixed geometry, each riding on a carrier atom with an isotropic displacement parameter amounting to 1.2 (1.5 for methyl H atoms) times the value of the equivalent isotropic parameter of the atom to which they are attached. The final R factors were $R = 0.0461$ for reflections with $I > 2\sigma(I)$ and $R = 0.0759$ for all data. Programs used were SIR-92 [15], SHELXL-97 [16], PARST [17], WinGX [18] and ORTEP3 [19].

2.6. Theoretical calculations

The potential energy surfaces (PES) for compound **8** with $C_S S_S$ configuration was performed using the GAUSSIAN 98 program [20], at the B3LYP/6-31g (d,p) level [21]. The PES calculation showed only one stable conformation for this compound with this configuration, the same result was found for the other diastereomer ($C_R S_S$). To get the stability for the other diastereomers, the configuration of carbon and sulphur were changed and their energies, geometries and IR frequencies were calculated at the B3LYP/6-31+g(d,p) level. The energies, geometric parameters and charges calculated for the $C_S S_S$ and $C_R S_S$ diastereomers which correspond to the more stable conformations **I** and **II**, respectively, are shown in Tables 5–7.

3. Results and discussion

Tables 1 and 2 present the stretching frequencies and the absorbance percentage of the analytically resolved carbonyl bands of the *meta-* (**1–6**) and *para-* (**7–12**) substituted α-methylsulfinyl-α-diethoxyphosphorylacetophenones, respectively. The frequencies of the corresponding *meta-* (**13–18**) and *para-* (**19–24**) substituted acetophenones are also presented in Tables 1 and 2, respectively, for comparison. Compounds **1–6** and **7–12** show doublets in all solvents. The intensity of the higher frequency doublet component, relative to the lower one, increases progressively on going from carbon tetrachloride to chloroform, and from these to acetonitrile, in the same way as the solvent polarity increases, for both series of compounds. These solvent effects and the occurrence of two carbonyl bands in the first overtone region at frequencies ca. twice those of the fundamental, and with about the same intensity ratios, strongly suggest that compounds **1–6** and **7–12** present, in solution, two stable conformers [22,23] (see below). The solvent effect on the carbonyl band components for **1** and **10**, as prototypes for the *meta-* and *para*-series, is illustrated in Figs. 1 and 2, respectively. However, taking into account, that the title compounds present two chiral centres, i.e. the α-methine carbon (C_R and C_S) and the sulfinyl sulfur (S_R and S_S) atoms, a racemic mixture of two pairs of diastereomers [($C_R S_R$; $C_S S_S$) and ($C_S S_R$; $C_R S_S$)] should be expected in solution as they have been synthesised without asymmetrical induction. Therefore, throughout the text, the $C_S S_S$ diastereomer, which corresponds to conformer **I**, should be also indistinctly designated either as ($C_S S_S, C_R S_R$)

Table 1

Frequencies (ν, cm^{-1}) and intensities of the carbonyl stretching bands in the IR spectra of α-methylsulfinyl-α-diethoxyphosphoryl-*meta*-substituted acetophenones m-Y-φ-C(O)CH[S(O)CH$_3$][P(O)(OCH$_2$CH$_3$)$_2$] (**1–6**) and the frequencies of the reference m-substituted acetophenones (**13–18**)

Comp.	Y	CCl$_4$				CHCl$_3$		CH$_3$CN	
		ν	P[a]	ν[b]	P	ν	P	ν	P
1	OMe	1682.5	28.9	3344.1	36.2	1677.2	48.6	1678.4	70.3
		1668.9	71.1	3317.7	63.8	1666.6	51.4	1668.3	29.7
13		1689.3				1682.1		1685.9	
2	Me	1680.0	36.1	3340.6	42.1	1676.2	64.3	1677.7	67.9
		1667.2	63.9	3315.2	57.9	1665.1	35.7	1668.0	32.1
14		1689.4				1680.6		1684.5	
3	F	1685.9	39.5	3352.1	48.0	1685.2	49.0	1683.5	70.0
		1672.3	60.5	3324.4	52.0	1673.5	51.0	1673.0	30.0
15		1695.7				1688.3		1691.3	
4	Cl	1685.5	41.7	3354.3	47.8	1685.2	44.1	1683.8	66.2
		1671.6	58.3	3324.9	52.2	1673.8	55.9	1673.1	33.8
16		1695.6				1688.5		1691.4	
5	Br	1686.5	43.0	3353.1	42.4	1684.1	60.6	1684.5	65.8
		1671.4	57.0	3323.4	57.6	1670.8	39.4	1672.9	34.2
17		1695.1				1688.0		1690.9	
6	NO$_2$	1691.7	43.6	3361.7	44.3	1691.0	46.3	1687.2	75.6
		1677.5	56.4	3334.6	55.7	1679.3	53.7	1676.5	24.4
18		1700.7				1695.3		1696.2	

[a] Intensity of each component of the carbonyl doublet expressed in percentage of absorbance.
[b] First overtone.

Table 2
Frequencies (ν, cm^{-1}) and intensities of the carbonyl stretching bands in the IR spectra of α-methylsulfinyl-α-diethoxyphosphoryl-*para*-substituted acetophenones *p*-Y-ϕ-C(O)CH[S(O)CH$_3$][P(O)(OCH$_2$CH$_3$)$_2$] (**7–12**) and the frequencies of the reference *p*-substituted acetophenones (**19–24**)

Comp.	Y	CCl$_4$				CHCl$_3$		CH$_3$CN	
		ν	P[a]	ν[b]	P	ν	P	ν	P
7	OMe	1674.8	39.4	3324.8	39.7	1669.6	51.4	1669.4	66.7
		1660.8	60.6	3302.7	60.3	1658.2	48.6	1659.5	33.3
19		1683.2				1673.8		1678.2	
8	H	1681.6	34.6	3345.1	33.3	1679.6	56.1	1679.6	64.0
		1671.3	65.4	3319.0	66.7	1669.7	43.9	1670.9	36.0
20		1691.2				1683.0		1685.9	
9	F	1683.0	32.0	3343.2	33.3	1679.4	52.2	1679.3	69.7
		1669.4	68.0	3319.5	67.7	1668.1	47.8	1669.1	30.3
21		1691.8				1685.2		1686.8	
10	Cl	1682.0	31.5	3345.7	46.5	1680.4	45.0	1680.2	56.0
		1668.0	69.5	3317.1	53.5	1668.0	54.0	1668.3	44.0
22		1692.0				1685.6		1687.5	
11	Br	1684.2	28.9	3345.1	52.0	1681.8	35.5	1680.0	73.0
		1669.1	71.1	3317.9	68.0	1668.0	64.5	1669.0	27.0
23		1693.6				1685.4		1687.7	
12	NO$_2$	1691.2	40.8	3359.8	40.1	1689.0	52.8	1688.1	70.8
		1676.3	59.2	3334.3	59.9	1676.7	47.2	1678.4	29.2
24		1700.5				1695.2		1697.1	

[a] Intensity of each component of the carbonyl doublet expressed in percentage of absorbance.
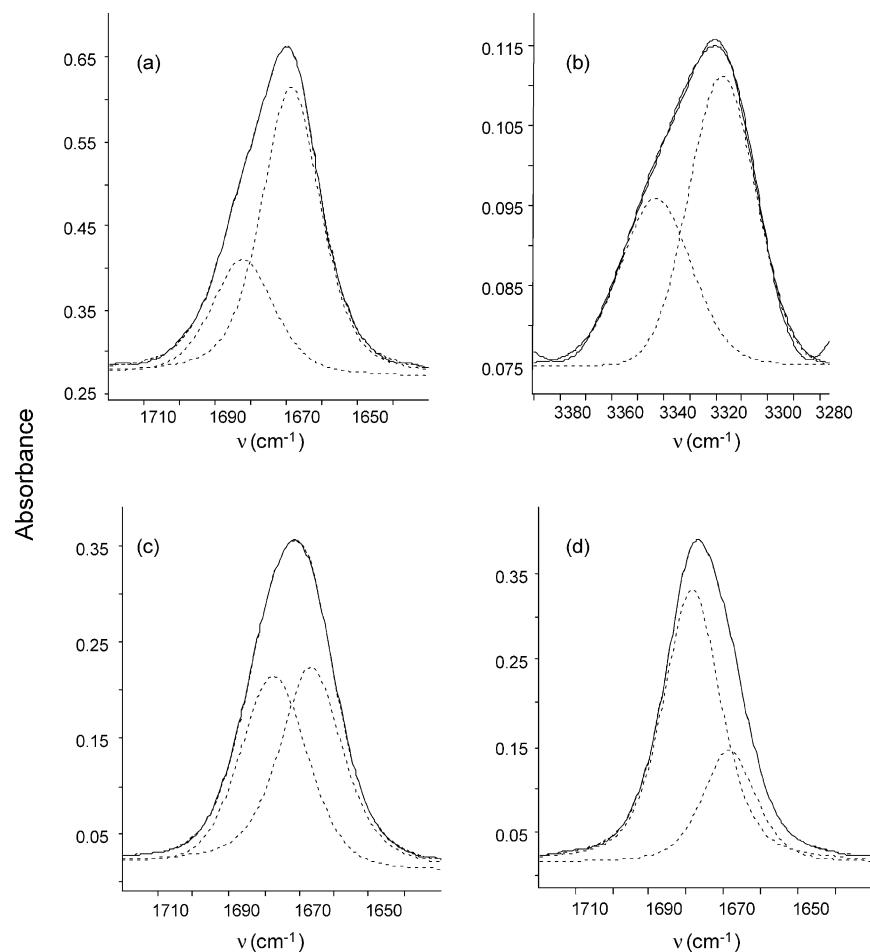[b] First overtone.

Fig. 1. IR spectra of *meta*-methoxy-α-methylsulfinyl-α-diethoxyphosphorylacetophenone (**1**) showing the analytically resolved carbonyl stretching bands, in carbon tetrachloride [fundamental (a) and first overtone (b)], chloroform (c) and acetonitrile (d).

Fig. 2. IR spectra of *para*-chloro-α-methylsulfinyl-α-diethoxyphosphorylacetophenone (**10**) showing the analytically resolved carbonyl stretching bands, in carbon tetrachloride [fundamental (a) and first overtone (b)], chloroform (c) and acetonitrile (d).
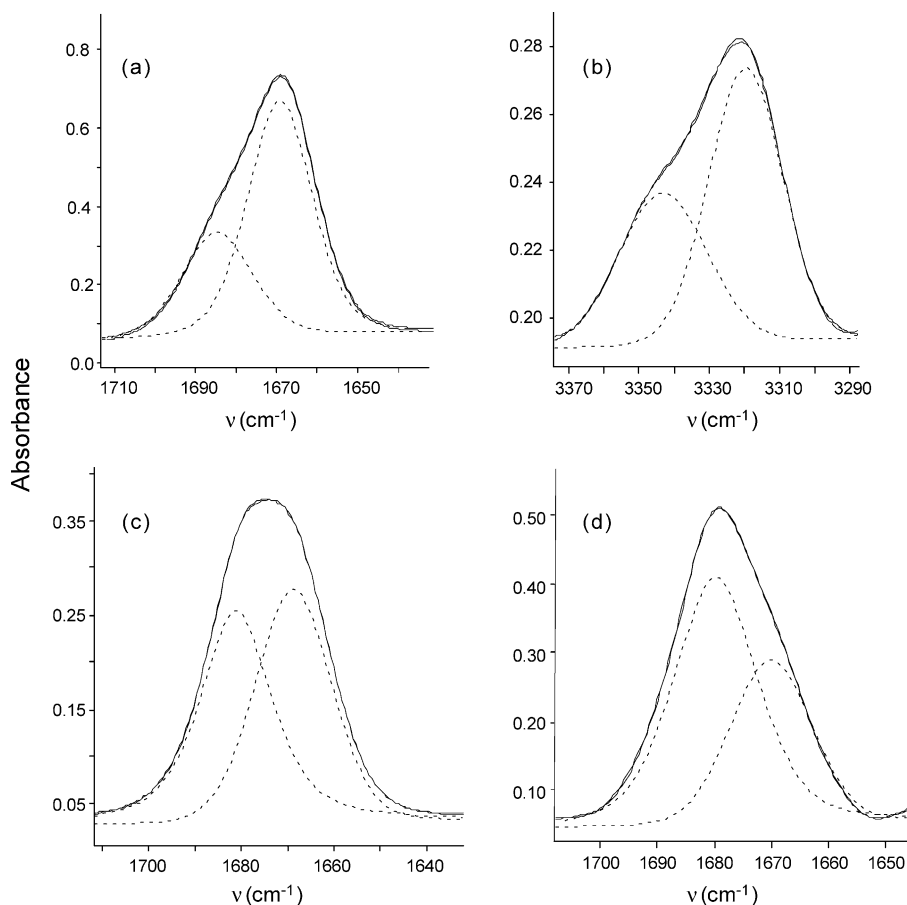
enantiomeric pair, which corresponds to the conformer pair (**I**), or sometimes called simply conformer (**I**). In the same way, the $C_R S_S$ diastereomer which corresponds to conformer **II** should be also designated either as ($C_R S_S, C_S S_R$) enantiomeric pair, which corresponds to the conformer pair (**II**), or sometimes called simply conformer (**II**).

In fact, the ^{1}H NMR spectra analyses clearly show the existence of the diastereomeric mixture for the title compounds. Fig. 3(a) is an illustrative example of the duplication of the methylsulfinyl [CH$_3$S(O)] singlet and α-methine [CH] doublet NMR signals in the spectrum of compound **1**, in CDCl$_3$. These signals, which correspond to the racemic mixtures of the diastereomeric pair (diast.$_1$ and diast.$_2$) for derivatives **1** and **10**, taken as representative examples of both series, in CCl$_4$, CDCl$_3$ and CD$_3$CN, are shown in Table 3. It may be observed, that the downfield [CH] doublet signal ($\delta \sim 5.45$ ppm) for diast.$_1$ is only slightly separated from the upfield signal mean value ($\delta \sim 5.40$ ppm) for diast.$_2$, by ca. 15 Hz. On the other hand, the downfield [CH$_3$S(O)] singlet signal ($\delta \sim 3.03$ ppm) for diast.$_1$ is significantly separated from the upfield signal ($\delta \sim 2.78$ ppm) for diast.$_2$, by ca. 75 Hz.

The concentrations of the two diastereomers (diast.$_1$ and diast.$_2$) of the racemic mixtures, for compounds **1**

and **10**, were estimated from the integrated intensities of both methylsulfinyl NMR signals, in CCl$_4$, CDCl$_3$ and CD$_3$CN solutions, and are in very good agreement with the data obtained from the infrared spectra (Table 4), which allowed the assignment of the correspondence between the downfield signal of diast.$_1$ with the higher ν_{CO} doublet frequency component. It may be noticed, from this table, that there is a progressive increase of the concentration of the diast.$_1$ with respect to diast.$_2$ as the polarity of the solvent increases, that is, it changes from ca. 30% (CCl$_4$) to 48% (CDCl$_3$) and to ca. 57% (CD$_3$CN) for diast.$_1$, while the corresponding decrease occurs for diast.$_2$. Fig. 4(a) and (b) illustrates well this behaviour for compounds **1** and **10**, respectively.

The above results suggest that diast.$_2$ is transformed into diast.$_1$, as the solvent relative permittivity increases, due to the inversion of the configuration of the α-carbon atom through a fast keto–enol equilibrium. Scheme 2 shows the equilibration of the $C_R S_S$ into the $C_S S_S$ diastereomer, through the intermediate enolic form [the same occurs with the other diastereomer pair ($C_S S_R$; $C_R S_R$)]. This proposal has been fully proved by the almost complete exchange of the α-methine hydrogen atom, of derivative **1**, by deuterium on treatment with deuterium oxide in neutral
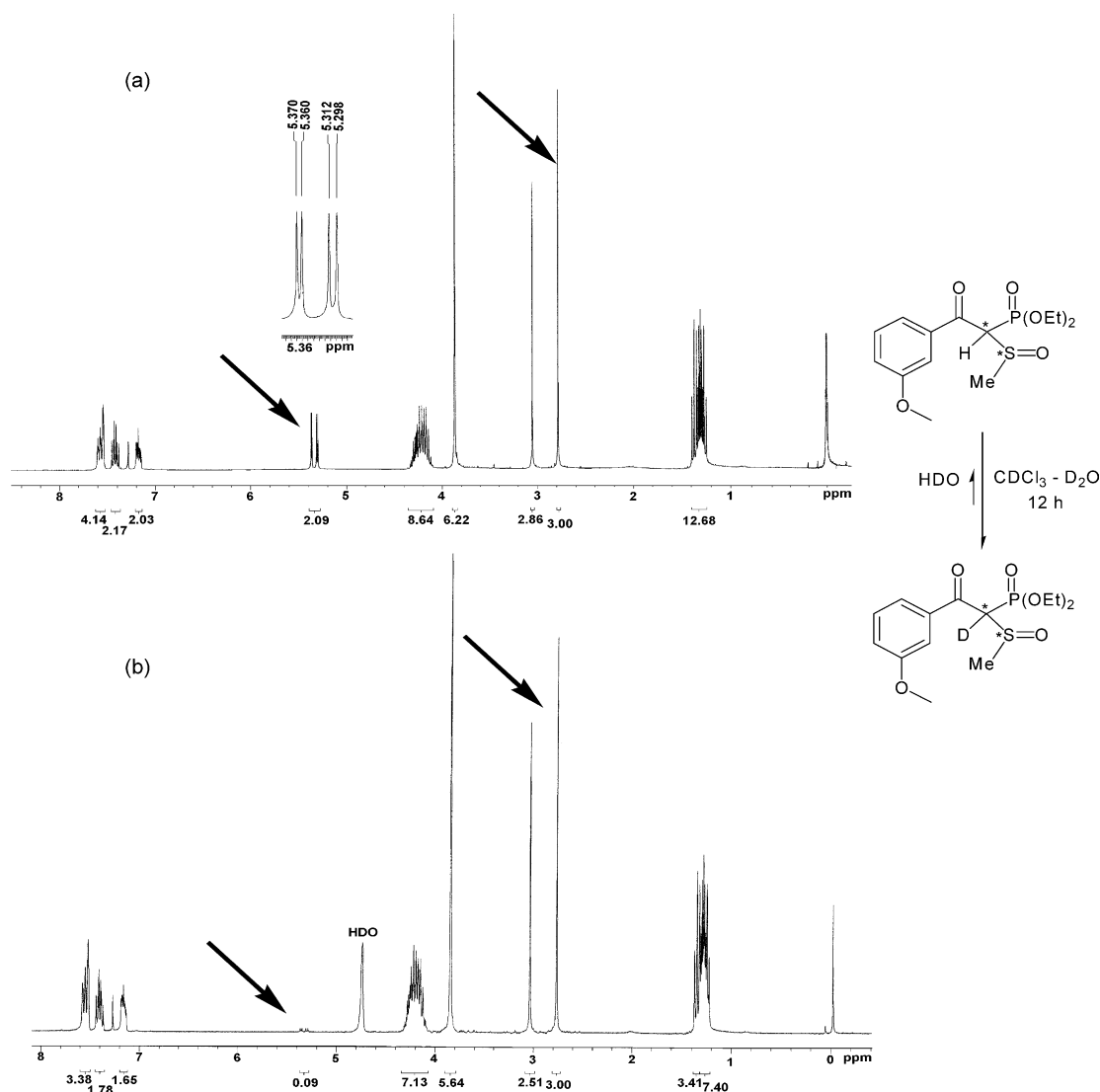
Fig. 3. ^{1}H NMR spectra of *meta*-methoxy-α-methylsulfinyl-α-diethoxyphosphorylacetophenone (**1**), in CDCl$_3$, showing: (a) the duplication of the methylsulfinyl [**CH$_3$**S(O)] singlet and α-methine (**CH**) doublet signals for the diastereomeric pair (diast.$_1$ and diast.$_2$); (b) the almost complete suppression of the α-methine (**CH**) signal due to deuteration.

deuterochloroform solution (see Section 2). Fig. 3(b) shows the almost disappearance of the α-methine ^{1}H NMR signal after deuteration, in comparison with Fig. 3(a).

Aiming to determine the geometric data of the more stable conformation, for each of two diastereomers, for

the series **1–6** and **7–12**, the B3LYP/6-3 + g(d,p) computations on the C$_S$S$_S$ and C$_R$S$_S$ diastereomers of the α-methylsulfinyl-α-diethoxyphosphorylacetophenone (**8**), taken as a representative compound, were performed. The same geometric parameters were found for the calculations

Table 3
Methylsulfinyl and methyne ^{1}H NMR signals for the racemic mixtures of the diastereomeric pair (diast.$_1$) and (diast.$_2$), for compounds **1** and **10**

Comp.	Y	CCl$_4$				CDCl$_3$				CD$_3$CN			
		diast.$_1$[a]		diast.$_2$[b]		diast.$_1$		diast.$_2$		diast.$_1$		diast.$_2$	
		δ_{Me}[c]	δ_{CH} ($^2J_{HP}$)[d]	δ_{Me}	δ_{CH} ($^2J_{HP}$)	δ_{Me}	δ_{CH} ($^2J_{HP}$)	δ_{Me}	δ_{CH} ($^2J_{HP}$)	δ_{Me}	δ_{CH} ($^2J_{HP}$)	δ_{Me}	δ_{CH} ($^2J_{HP}$)
1	*m*-MeO	3.19	5.46 (18.1)	2.89	5.36 (18.9)	3.05	5.39 (17.4)	2.78	5.32 (18.6)	2.94	5.60 (17.1)	2.71	5.54 (18.8)
10	*p*-Cl	2.98	5.31 (17.7)	2.70	5.28 (18.9)	3.06	5.32 (18.9)	2.79	5.28 (17.1)	3.00	5.64 (17.4)	2.78	5.60 (19.2)

[a] Refer to C$_R$S$_S$ (Conformer **II**) (see Table 5).
[b] Refer to C$_S$S$_S$ (Conformer **I**) (see Table 5).
[c] In ppm relative to TMS.
[d] In Hz.

Table 4
Relative concentrations[a] of the racemic mixtures of diastereomeric pairs (diast.$_1$)[b] and (diast.$_2$)[c] for compounds **1** and **10**, estimated from the integrated intensity of the methylsulfinyl ^{1}H NMR signal

Comp.	Y	CCl$_4$		CDCl$_3$		CD$_3$CN	
		diast.$_1$[d]	diast.$_2$[e]	diast.$_1$	diast.$_2$	diast.$_1$	diast.$_2$
1	*m*-MeO	29.9 (29)[f]	70.1 (71)[g]	49.3 (48)	50.7 (52)	57.5 (70)	42.5 (30)
10	*p*-Cl	31.2 (31)	68.8 (69)	45.7 (45)	54.3 (54)	56.3 (56)	43.7 (44)

[a] Expressed in molar fraction of the racemic mixtures of each diastereomer.
[b] Refer to C$_R$S$_S$ (Conformer **II**) (see Table 5).
[c] Refer to C$_S$S$_S$ (Conformer **I**) (see Table 5).
[d] diast.$_1$ correspond to the downnfield ($\delta \sim 3.03$ ppm) methylsulfinyl ^{1}H NMR signal (Table 3).
[e] diast.$_2$ correspond to the upfield ($\delta \sim 2.78$ ppm) methylsulfinyl ^{1}H NMR signal (Table 3).
[f] Molar fraction of the higher IR frequency components of the carbonyl doublet (Tables 1 and 2).
[g] Molar fraction of the lower IR frequency components of the carbonyl doublet (Tables 1 and 2).
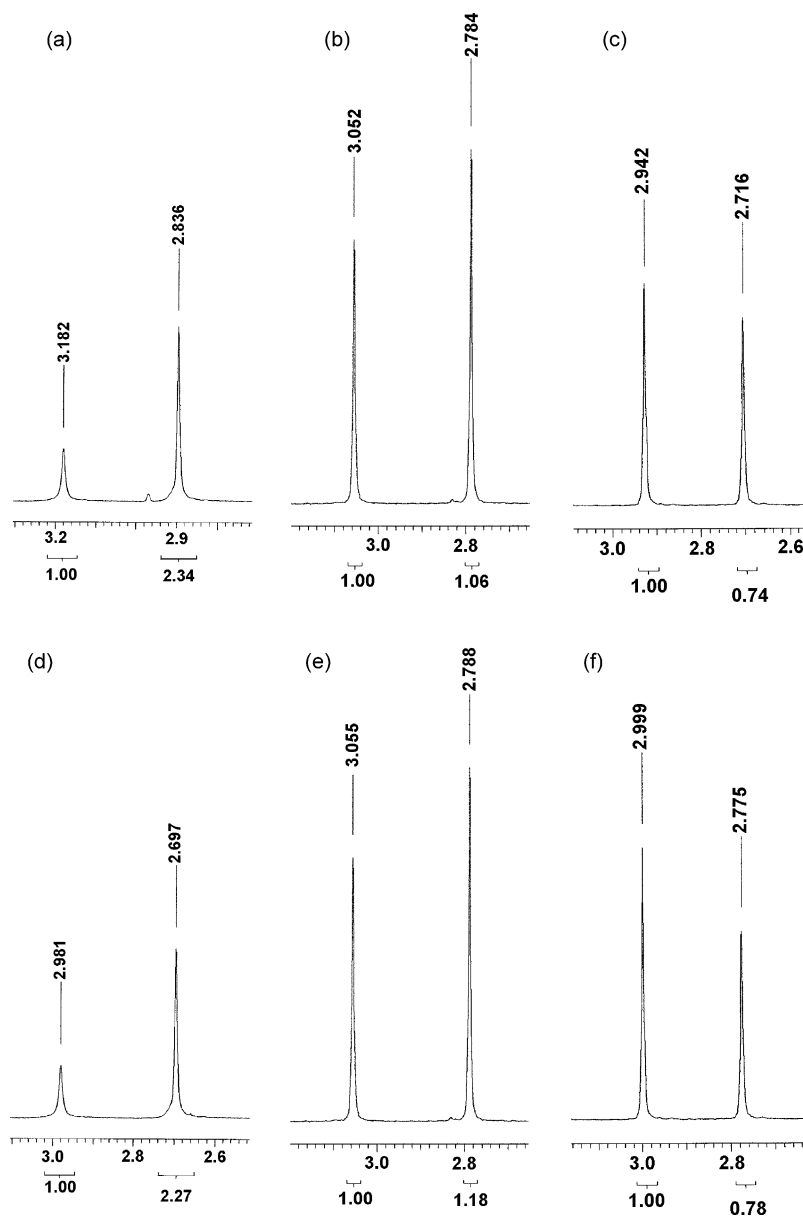

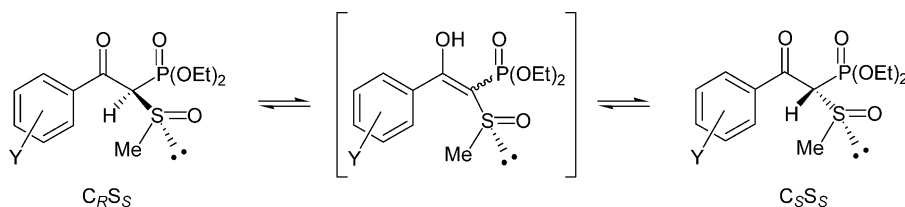Fig. 4. ^{1}H NMR methylsulfinyl [**CH**$_3$S(O)] singlet signal for the diastereomeric pair (diast.$_1$ and diast.$_2$) of *meta*-methoxy- (**1**) and *para*-chloro-α-methylsulfinyl-α-diethoxy-phosphorylacetophenone (**10**) in: carbon tetrachloride (a, d), deuterochloroform (b, e) and deuteroacetonitrile (c, f), respectively, showing the solvent effect on the relative intensities of each diastereomer.

Scheme 2.

performed for the corresponding enantiomers (C_RS_R and C_SS_R) diastereomeric pair.

Table 5 shows the relevant data for compound **8**, along with the X-ray dihedral angles for compound **1**. The more stable and less polar C_SS_S diastereomer (conformer **I**) displays the [MeS(O)] group ($\alpha' = 35.1°$) in a *quasi-syn-periplanar* (*quasi-cis*) geometry and the [P(O)(OEt)$_2$] group ($\alpha' = -99.6°$) in a *anti-clinal* (*gauche*) geometry relative to the carbonyl group (Structure **I**, Scheme 3). The less stable and more polar C_RS_S diastereomer (conformer **II**) presents the [MeS(O)] group ($\alpha' = -47.9°$) and the [P(O)(OEt)$_2$] group ($\alpha' = -86.4°$) in a *syn-clinal* (*gauche*) geometry relative to the carbonyl group (Structure **II**, Scheme 3). Data from Table 5 shows that the less stable and more polar diastereomer C_RS_S (conformer **II**) presents the higher carbonyl calculated frequency (1747 cm^{-1}), while the more stable and less polar diastereomer C_SS_S (conformer **I**) presents the lower carbonyl calculated frequency (1725 cm^{-1}). These data are in perfect agreement with the experimental IR data for compounds **1–6** and **7–12**, in the non-polar solvent carbon tetrachloride (Tables 1 and 2), indicating that the higher carbonyl doublet frequency component corresponds to the less stable and more polar C_RS_S diastereomer (diast.$_1$), while the lower frequency component corresponds to the more stable and less polar C_SS_S diastereomer (diast.$_2$).

The geometry of conformation **I** (Scheme 3), which corresponds to the more stable C_SS_S diastereomer, indicates that there is a very short intramolecular contact between the oppositely charged carbonyl oxygen ($-0.548e$) and the positively charged sulfur ($+0.984e$) atoms (Table 7), which is responsible for strong $O^{\delta-}_{(CO)}\cdots S^{\delta+}_{(SO)}$ electrostatic and CT interactions. In fact, this contact is not only significantly shorter than the sum of the van der Waals ($\sum vdW$) radii by 0.54 Å (Table 6), but also shorter than the same contact

found in the *cis* conformers of the previously studied α-ethylsulfinylacetophenones [7,8,24]. Additionally, this conformation is stabilised almost into the same extent by two electrostatic interactions (hydrogen bonds): (a) between one of the positively charged methylsulfinyl hydrogen $H^{\delta+}_{a\,(CH_3SO)}$ ($+0.195e$) and the negatively charged ethoxyphosphoryl oxygen $O^{\delta-}_{(POEt)}$ ($-0.771e$) atoms, whose intramolecular contact $O^{\delta-}_{(POEt)}\cdots H^{\delta+}_{a\,(CH_3SO)}$ is 0.28 Å shorter than the $\sum vdW$ radii; (b) between a second positively charged methylsulfinyl hydrogen $H^{\delta+}_{b\,(CH_3SO)}$ ($+0.196e$) and the negatively charged carbonyl oxygen $O^{\delta-}_{(CO)}$ ($-0.548e$) atoms, being their intramolecular contact $O^{\delta-}_{(CO)}\cdots H^{\delta+}_{b\,(CH_3SO)}$ 0.24 Å shorter than the $\sum vdW$ radii.

Conformation **II** (Scheme 3), which corresponds to the less stable C_RS_S diastereomer, allows two short contacts: (a) between the negatively charged carbonyl oxygen $O^{\delta-}_{(CO)}$ ($-0.567e$) and the positively charged sulfinyl sulfur $S^{\delta+}_{(SO)}$ ($+1.019e$) atoms, whose interatomic distance $O^{\delta-}_{(CO)}\cdots S^{\delta+}_{(SO)}$ is 0.14 Å shorter than the $\sum vdW$ radii; (b) between the negatively charged sulfinyl oxygen atom $O^{\delta-}_{(SO)}$ ($-0.808e$) and the positively charged carbonyl carbon $C^{\delta+}_{(CO)}$ ($+0.572e$) atoms, being their interatomic distance $O^{\delta-}_{(SO)}\cdots C^{\delta+}_{(CO)}$ 0.09 Å shorter than the $\sum vdW$ radii. Both contacts originate only moderate crossed $O^{\delta-}_{(CO)}\cdots S^{\delta+}_{(SO)}$ and $O^{\delta-}_{(SO)}\cdots C^{\delta+}_{(CO)}$ electrostatic and CT interactions. Additionally, conformation **II** is stabilised by strong $H^{\delta+}_{(CH_3SO)}\cdots O^{\delta-}_{(CO)}$ electrostatic (hydrogen bond) interaction between the positively charged methylsulfinyl hydrogen $H^{\delta+}_{(CH_3SO)}$ ($+0.224e$) and the negatively charged carbonyl oxygen $O^{\delta-}_{(CO)}$ ($-0.567e$) atoms, whose intramolecular contact is 0.43 Å shorter than the $\sum vdW$ radii.

It should be pointed out, that conformers **I** and **II** are further stabilised, into almost the same extent, by: (a) the $O^{\delta-}_{(POEt)}\cdots C^{\delta+}_{(CO)}$ electrostatic and CT interaction between the negatively charged ethoxyphosphoryl oxygen $O^{\delta-}_{(POEt)}$

Table 5
Relative energy (E, kJ/mol), dipole moments (μ, Da), carbonyl frequencies (ν_{CO}, cm^{-1}) and selected dihedral angles (deg) optimized for the minimum energy conformations of diastereomers C_SS_S and C_RS_S, for compound **8**, at the B3LYP/6-31+g(d,p) level, and the X-ray geometrical data for compound **1**

Comp.	Conf.[a]	E	μ	ν_{CO}	Dihedral angles[b]									
					α	α'	β	β'	γ	γ'	γ''	δ	δ'	ϕ
8	**I** (C_SS_S)[c]	0.0	2.9	1725.1	−99.6	35.1	−84.4	164.9	41.3	148.0	−83.3	87.9	−171.2	−8.6
	II (C_RS_S)	12.5	4.4	1746.9	86.4	−47.9	82.8	−45.2	−44.8	−151.4	66.3	94.6	−171.2	19.8
1	**II**′(C_RS_S) X-ray				80.6(2)	−40.9(2)	160.7(1)	−169.7(1)	32.38(14)	−74.18(14)	−60.2(2)	101.4(2)	−179.7(2)	−22.2(3)

[a] Conformer designation.
[b] Configuration specification of the α-carbon and sulfur chiral atoms.
[c] See Scheme 1.
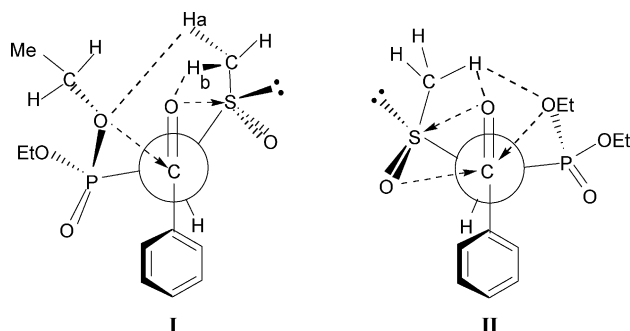
Scheme 3.

(ca. $-0.75e$) and the positively charged carbonyl carbon $C^{\delta+}_{(CO)}$ (ca. $+0.59e$) atoms, whose intramolecular contact is 0.22 Å shorter than the $\sum vdW$ radii; (b) the $H^{\delta+}_{(o-Ph)}\cdots O^{\delta-}_{(CO)}$ electrostatic interaction (hydrogen bond) between the positively charged *ortho*-hydrogen $H^{\delta+}_{(o-Ph)}$ (ca. $+0.21e$) and the negatively charged $O^{\delta-}_{(CO)}$ (ca. $-0.57e$) atoms, whose intramolecular contact is 0.29 Å shorter than the $\sum vdW$ radii.

From the above analysis, it seems reasonable to conclude, that the summing up of the interactions, which stabilise conformer **I**, are more pronounced than those which stabilise conformer **II**. Moreover, the $O^{\delta-}_{(CO)}\cdots S^{\delta+}_{(SO)}$ orbital and electronic interactions seems to be of paramount importance for the larger stabilisation of conformer **I** with respect to conformer **II**, while the remainder

electronic interactions $O^{\delta-}_{(POEt)}\cdots C^{\delta+}_{(CO)}$, $O^{\delta-}_{(POEt)}\cdots H^{\delta+}_{a\,(CH_3-SO)}$, $O^{\delta-}_{(CO)}\cdots H^{\delta+}_{b\,(CH_3SO)}$ and $O^{\delta-}_{(CO)}\cdots H^{\delta+}_{(o-Ph)}$, which stabilise conformer **I**, are almost equivalent to the electronic interactions $O^{\delta-}_{(CO)}\cdots S^{\delta+}_{(SO)}$, $O^{\delta-}_{(SO)}\cdots C^{\delta+}_{(CO)}$, $O^{\delta-}_{(POEt)}\cdots C^{\delta+}_{(CO)}$, $O^{\delta-}_{(CO)}\cdots H^{\delta+}_{(CH_3SO)}$ and $O^{\delta-}_{(CO)}\cdots H^{\delta+}_{(o-Ph)}$, which stabilise the conformer **II**.

A further evidence for the $O^{\delta-}_{(CO)}\cdots S^{\delta+}_{(SO)}$ CT interaction, which occurs in conformer **I**, can be obtained from the charge analysis for some relevant atoms (Table 7). The larger negative charge of the $O^{\delta-}(7)_{[POEt]}$ atom ($-0.771e$), which is located slightly closer to the carbonyl carbon atom in conformer **I**, relative to the same contact for conformer **II**, induces a larger $C^{\delta+}_{(CO)}$ positive charge ($0.604e$) for **I**, relative to that of **II** ($0.572e$). Consequently, it should be expected an increased $O^{\delta-}(1)_{[CO]}$ negative charge for **I**, with respect to that for **II**. Nevertheless, an inverse trend is observed due to the $O^{\delta-}_{(CO)}\cdots S^{\delta+}_{(SO)}$ CT interaction in conformer **I**, that is the $O^{\delta-}(1)_{[CO]}$ charge for **I** ($-0.548e$) is smaller than that for **II** ($-0.567e$) and the $S^{\delta+}(8)_{[SO]}$ positive charge for **I** ($0.984e$) is smaller than that for **II** ($1.019e$).

Moreover, contrarily to what should be expected, the $O^{\delta-}(9)_{[SO]}$ negative charge for **I** is not increased relative to that of **II**. This reverse trend may be easily explained taking into account, that there is a shorter contact between the $H^{\delta+}(3)_{(\alpha-CH)}$ positively charged methine hydrogen atom and the $O^{\delta-}(9)_{[SO]}$ atom for **II** (2.751 Å), with respect to

Table 6

Selected interatomic distances (Å) for the minimum energy conformations of diastereomers C_SS_S and C_RS_S, obtained at the B3LYP/6-31+g(d,p) level for compound **8**, and the X-ray geometrical data for compound **1**

Comp.	Conf.[a]	Interatomic distances[b]								
		$O(1)\cdots$ $S(8)$[c]	$O(1)\cdots$ $P(4)$[c]	$O(9)\cdots$ $C(2)$[d]	$O(6)\cdots$ $S(8)$[c]	$O(9)\cdots$ $P(4)$[c]	$O(1)\cdots$ $H_b(10)$[e,f]	$O(7)\cdots$ $H_a(10)$[e,f]	$O(7)\cdots$ $C(2)$[d]	$O(1)\cdots$ $H(2')$[e]
8	**I** (C_SS_S)[g]	2.789	3.593	4.023	3.816	3.594	2.484	2.445	2.988	2.447
	II (C_RS_S)	3.188	3.506	3.135	3.765	4.394	2.299	2.844	3.058	2.499
1	**II**′(C_RS_S) X-ray	2.988(2)	3.340(2)	3.955(3)	3.038(2)	3.334(2)	2.79	5.40	2.911(3)	2.52(97.4°)[h]

[a] Conformer designation.

[b] See Scheme 1.

[c] Sum of the van der Waals raddi = 3.32 Å.

[d] Sum of the van der Waals raddi = 3.22 Å.

[e] Sum of the van der Waals raddi = 2.72 Å.

[f] Refers to the contact between the carbonyl oxygen and the nearest methylsulfinyl hydrogen atom.

[g] Configuration specification of the α-carbon and sulfur chiral atoms.

[h] Refers to the C(2′)–H⋯O(1) angle (in degrees).

Table 7

Charges (e) at selected atoms[a] obtained at the B3LYP/6-31+g(d,p) level for compound **8**

Conf.[b]	$O(1)_{[CO]}$	$C(2)_{[CO]}$	$O(9)_{[SO]}$	$S(8)_{[SO]}$	$O(5)_{[PO]}$	$P(4)_{[PO]}$	$O(7)_{[POEt]}$	$O(6)_{[POEt]}$	$H(10)_{[Me]}$[c]	$H(3)_{[CH]}$	$H(2')_{[o-Ph]}$
I (C_SS_S)[d]	-0.548[e]	0.604	-0.781	0.984	-0.742	1.687	-0.771	-0.736	0.181	0.215	0.196
II (C_RS_S)	-0.567	0.572	-0.808	1.019	-0.746	1.708	-0.748	-0.767	0.184	0.220	0.197

[a] See Scheme 1.

[b] Conformer designation.

[c] Refers to the mean charge value for the three methyl hydrogen atoms.

[d] Configuration specification of the α-carbon and sulfur chiral atoms.

[e] A minus sign indicates an excess of negative charge.

Table 8
Carbonyl frequency shifts[a] ($\Delta\nu$, cm^{-1}) for the diastereomeric pairs (conformer **I**) and (conformer **II**) of compounds **1–6** and **7–12**

Comp.	Y	CCl$_4$	CHCl$_3$	Comp.	Y	CCl$_4$	CHCl$_3$
1	*m*-MeO	−6.8[b]	−4.9	**7**	*p*-MeO	−8.4	−4.2
		−20.4[c]	−15.5			−22.4	−15.6
2	*m*-Me	−9.4	−4.4	**8**	**H**	−9.6	−3.4
		−22.2	−15.5			−19.9	−13.3
3	*m*-F	−9.8	−3.1	**9**	*p*-F	−8.0	−3.9
		−23.4	−14.8			−21.6	−15.2
4	*m*-Cl	−10.1	−3.3	**10**	*p*-Cl	−10.0	−5.2
		−24.0	−15.7			−24.0	−17.6
5	*m*-Br	−8.6	−3.9	**11**	*p*-Br	−9.4	−3.6
		−23.7	−17.2			−24.5	−17.4
6	*m*-NO$_2$	−9.0	−4.3	**12**	*p*-NO$_2$	−8.8	−6.2
		−23.2	−16.0			−23.7	−18.5

[a] $\Delta\nu$ refers to the difference: $\nu_{\{m,p\text{-}Y\text{-}\phi\text{-}C(O)CH[SOMe][P(O)(OEt)_2]\}} - \nu_{[m,p\text{-}Y\text{-}\phi\text{-}C(O)CH_3]}$.

[b] Refer to conformer **II** (C_RS_S, C_SS_R).

[c] Refer to conformer **I** (C_SS_S, C_RS_R).

the same contact for **I** (2.920 Å), which, in turn, induces a larger O$^{\delta-}$(9)$_{[SO]}$ negative charge for **II** ($-0.808e$), relative to that for **I** ($-0.781e$). Consequently, the positively charged methine hydrogen atom H$^{\delta+}$(3)$_{(\alpha\text{-CH})}$ for **II** (0.220e) is slightly increased relative to that for **I** (0.215e).

The unusual strong O$^{\delta-}_{(CO)}\cdots$S$^{\delta+}_{(SO)}$ CT for conformer **I**, which brings the O$_{(CO)}$ and the S$_{(SO)}$ atoms closer to each other, with respect to conformer **II**, is also responsible for the smaller O=C–C (118.3°) and C–C–S (108.1°) angles for conformer **I**, in comparison to the O=C–C (120.3°) and C–C–S (113.1°) angles for conformer **II**.

It is worth to note that the downfield α-methine and methylsulfinyl hydrogen signals (3.19 and 5.46 ppm for **1**, in CCl$_4$, respectively) to diast.$_2$ (conformer **I**) and the corresponding upfield signals (2.89 and 5.36 ppm, for **1**, in CCl$_4$, respectively) to diast.$_1$ (conformer **II**) (Table 3) are in good agreement with the computed slightly smaller positive charge for the methynic ($+0.215e$) and methyl ($+0.181e$) hydrogen atoms for conformer **I** (C_SC_S; C_RC_R) pair, relative to the corresponding hydrogen atoms ($+0.220e$ and $+0.184e$, respectively) for conformer **II** (C_RC_S; C_SC_R) (Table 7).

The above mentioned interactions, which are stronger for conformer **I** with respect to **II**, act lowering the carbonyl bond order and thus the ν_{CO} frequency into a larger extent for **I**, than for **II**. This rationalisation is in agreement with the lower computed ν_{CO} frequency (1725 cm^{-1}) for **I** relative to that for **II** (1747 cm^{-1}) (Table 5), and also with their larger relative negative carbonyl frequency shifts ($\Delta\nu$) (Table 8), for the conformer **I** relative to conformer **II**, along the *meta*- **1–6** and *para*- **7–12** series, with respect to the parent compounds **13–18** and **19–24**, in carbon tetrachloride and chloroform (Tables 1 and 2).

The significant negative and almost constant carbonyl frequency shift for conformer **I** ($\Delta\nu \approx -20$ cm^{-1}, in CCl$_4$; $\Delta\nu \approx -16$ cm^{-1}, in CHCl$_3$) and **II** ($\Delta\nu \approx -9$ cm^{-1}, in CCl$_4$; $\Delta\nu \approx -4$ cm^{-1}, in CHCl$_3$) (Table 8), for compounds of both *meta*- (**1–6**) and *para*-series (**7–12**), relative to

the parent acetophenones, are in line with the prevalence of the electronic interactions, which act decreasing the ν_{CO} frequency, over the summing up of the −I effect of the methylsulfinyl ($\sigma_I = 0.49$) [25] and the diethoxyphosphoryl ($\sigma_I = 0.33$) [25] groups, which should lead to a significant increase of the ν_{CO} frequency.

X-ray diffraction analysis was performed for the *meta*-methoxy-derivative **1**. The molecules, in the crystal, are present as centrosymmetric dimers (C_RS_S; C_SS_R enantiomeric pair), which are connected through an intricate network of electrostatic interactions (mostly hydrogen bonds). Fig. 5 displays the C_RS_S diastereomer for compound **1** and Tables 5 and 6 present its geometric parameters (conformer **II**′, Scheme 4). Fig. 5 also shows that the *meta*-O–CH$_3$ group possess an *anti* orientation relative to the carbonyl group and the methoxy methyl group deviates slightly from the benzene ring plane [$\omega = -10.5°$ (3) (see Scheme 1). The α and α′ dihedral angles of conformer **II**′ (C_RS_S; C_SS_R enantiomeric pair) for **1** in the single crystal are similar to the corresponding angles of the more polar
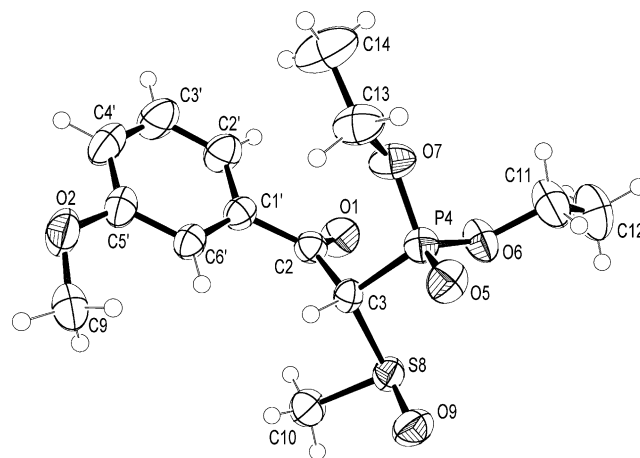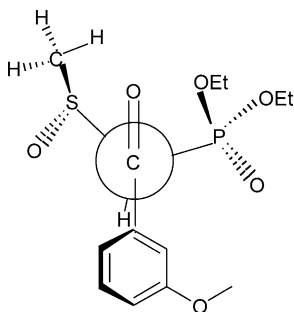

Fig. 5. X-ray crystal structure of the C_RS_S diastereomer of **1**, with atoms labelling. Displacement ellipsoids are drawn at 50% probability level and H atoms are shown as spheres of arbitrary radii.

II'

Scheme 4.

conformer **II** (enantiomeric pair $C_R S_S$; $C_S S_R$) for compound **8** in the gas phase. However the other torsional angles of **II'** differ significantly from those of **II**.

Conformer **II'** allows also several intramolecular short contacts between oppositely charged atoms, i.e. $O^{\delta-}(1)_{[CO]}\cdots S^{\delta+}(8)_{[SO]}$, $O^{\delta-}(7)_{[POEt]}\cdots C^{\delta+}(2)_{[CO]}$, and $O^{\delta-}(6)_{[POEt]}\cdots S^{\delta+}(8)_{[SO]}$, whose interatomic distances are ca. 0.30 Å shorter than the $\sum vdW$ radii of the relevant atoms. Additionally, the ϕ dihedral angle, of ca. $-22°$, allows a short contact between the $H^{\delta+}(8)_{[o\text{-}Ph]}\cdots O^{\delta+}(1)_{[CO]}$ atoms, whose interatomic distance is ca. 0.20 Å shorter than the $\sum vdW$ radii of their atoms, while the $O^{\delta-}(1)_{[CO]}\cdots P^{\delta+}(4)_{[PO]}$ and $O^{\delta-}(1)_{[CO]}\cdots H^{\delta+}_{[SOMe]}$ contacts are close to the corresponding $\sum vdW$ radii. Therefore, the summing up of these orbital and electrostatic interactions should contribute for the stabilisation of conformer **II'**, in the solid state. Further stabilisation derives from dipole moment coupling and several intermolecular electrostatic interactions (hydrogen bonds) among negatively charged oxygen atoms and relevant positive charged hydrogen atoms.

4. Conclusions

The ν_{CO} analysis (fundamental and first overtone) of the meta- (**1–6**) and para- (**7–12**) substituted α-methylsulfinyl-α-diethoxyphosphorylacetophenones suggests the existence of two stable conformers, in solution. Their ^{1}H NMR spectra clearly show that these two conformers correspond to two pairs of diastereomers ($C_S S_S$; $C_R S_R$) (diast.$_1$) and ($C_S S_S$; $C_R S_R$) (diast.$_2$) (racemic mixtures), whose occurrence is in agreement with the presence of two chiral centres (α-methine carbon and sulfinyl sulfur atoms). The concentrations of the two diastereomers have been estimated from the two ^{1}H NMR methylsulfinyl singlet signals. The progressive increase of the obtained molar fraction of diast.$_1$, relative to that of diast.$_2$, on going from CCl$_4$ to CDCl$_3$ and to CD$_3$CN, associated with the corresponding increase of intensity for the higher IR ν_{CO} frequency doublet component, for the same solvent series, relative to the lower frequency component, led to the conclusion that the former component corresponds to diast.$_1$, while the lower ν_{CO} frequency conformer corresponds to diast.$_2$.

Additionally, there is a good matching of the concentrations of diast.$_1$ and diast.$_2$ estimated by the two methods. i.e. NMR and IR spectroscopy, which, along with the complete deuterium exchange of the α-methine hydrogen atom of **1** in deuterium oxide, suggests that diast.$_1$ is transformed in diast.$_2$ as the solvent polarity increases, through a rapid keto–enol equilibrium.

The theoretical calculations at B3LYP/6-31 + g(d,p) level, performed for compound **8**, show that the more stable and less polar $C_S S_S$ diastereomer (conformer **I**) displays the [MeS(O)] group in a quasi-syn-periplanar (quasi-cis) geometry and the [P(O)(OEt)$_2$] group in an anti-clinal (gauche) geometry relative to the carbonyl group. The less stable and more polar $C_R S_S$ diastereomer (conformer **II**) presents the [MeS(O)] group and the [P(O)(OEt)$_2$] group in a syn-clinal (gauche) geometry relative to the carbonyl group.

The computed carbonyl frequencies, 1747 and 1725 cm^{-1}, corresponding to diastereomer $C_R S_S$ (conformer **I**) and to diastereomer $C_S S_S$ (conformer **II**), respectively, are in perfect agreement with our IR data for compounds **1–6** and **7–12**, in a non-polar solvent, carbon tetrachloride, indicating that the higher carbonyl doublet frequency component corresponds to $C_R S_S$ diastereomer (diast.$_1$), while the lower frequency to the more stable and less polar $C_S S_S$ diastereomer (diast.$_2$).

The larger stabilisation of conformer **I** ($C_S S_S$; $C_R S_R$ enantiomeric pair) over conformer **II** ($C_R S_S$; $C_S S_R$ enantiomeric pair) is mainly due to the very strong $O^{\delta-}_{(CO)}\cdots S^{\delta+}_{(SO)}$ CT and Coulombic interaction, which takes place in conformer **I**, while the remainder electronic interactions, which stabilise conformer **I**, are almost counterbalanced by the electronic interactions, which stabilise conformer **II**. This rationalisation is supported by the larger negative carbonyl frequency shifts ($\Delta\nu$) for **I** (ca. -20 cm^{-1}, in CCl$_4$), with respect to **II** (ca. -9 cm^{-1}, in CCl$_4$), for the meta- (**1–6**) and para-series (**7–12**), relative to the parent acetophenones, in spite of the strong $-I$ effect of the [S(O)Me] and [P(O)(OEt)$_2$] groups.

X-ray diffraction analysis of **1** shows that it is stabilised in the solid state in the conformation **II'** ($C_R S_S$; $C_S S_R$ enantiomeric pair), whose α and α' torsional angles are close to the corresponding angles of the more polar conformer **II** ($C_R S_S$; $C_S S_R$ enantiomeric pair), for compound **8**, in the gas phase. However, the other torsional angles for **II'** differ significantly from those of conformer **II**. The $O^{\delta-}_{(CO)}\cdots S^{\delta+}_{(SO)}$, $O^{\delta-}_{(POEt)}\cdots C^{\delta+}_{(CO)}$, $O^{\delta-}_{(POEt)}\cdots S^{\delta+}_{(SO)}$ and $O^{\delta-}_{(CO)}\cdots H^{\delta+}_{(o\text{-}Ph)}$ orbital and electrostatic intramolecular interactions contribute for the stabilisation of **II'**. The molecules in the crystal are present as centrosymmetric dimers, which in turn are connected through dipole moment coupling and by an intricate network of electrostatic interactions (hydrogen bonds).

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