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Comparative spectroscopic and theoretical studies on the conformation of some α-diethoxyphosphoryl carbonyl compounds and their α-ethylsulfonyl analogues[1]

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Comparative ν_{CO} IR analysis of β-carbonylphosphonates [XC(O)CH$_2$P(O)(OR)$_2$: X = Me **1**, Ph **2**, OEt **3**, NEt$_2$ **4** and SEt **5**; R = Et] (series **I**) and β-carbonylsulfones [XC(O)CH$_2$SO$_2$R: X = Me **6**, Ph **7**, OEt **8**, NEt$_2$ **9** and SEt **10**; R = Et] (series **II**) along with *ab initio* 6-31G** calculations on **1a** and **6a** (R = Me) suggest the existence of only a single *gauche* conformer for series **I**. The negative carbonyl frequency shifts for both series follow approximately the electron-affinities of the π^*_{CO} orbital of the parent compounds MeC(O)X **11**–**15**. The less positive asymmetric sulfonyl frequency shifts ($\Delta\nu_{SO_2}$) for **II** in relation to the phosphoryl frequency shifts ($\Delta\nu_{PO}$) for **I** and the larger negative carbonyl frequency shifts for **II** with respect to the corresponding values for **I** are in line with the upfield ^{13}C NMR chemical shifts of the carbonyl carbon for **II** compared to **I**. These trends agree with the shorter $O_{(SO_2)}\cdots C_{(CO)}$ contact in comparison with the $O_{(PO)}\cdots C_{(CO)}$ one and are discussed in terms of $O_{lp}\rightarrow\pi^*_{CO}$ charge transfer and electrostatic interactions, which are stronger for series **II** than for **I**, indicating that the sulfonyl oxygen atom is a better electron donor than the phosphoryl oxygen atom. Intrinsic geometrical parameters of O=S–CH$_2$ and O=P–CH$_2$ moieties seem to be responsible for this behaviour as indicated by X-ray study and *ab initio* calculations of dialkyl (methylsulfonyl)methylphosphonate MeSO$_2$CH$_2$P(O)(OR)$_2$ (R = Et **18**, Me **18a**).

Our previous spectroscopic (IR, ^{13}C NMR, UV and UPS), X-ray diffraction and theoretical studies of some β-carbonylsulfides and -sulfones XC(O)CH$_2$SO$_n$R[2–13] (X = Me, Ar, NR$_2$, OR and SR; R = Me, Ar; n = 0 and 2) indicated that these compounds in the gas phase, in solution and in the solid state (for the β-carbonylsulfones) prefer a *gauche* conformation between the C=O and CH$_2$–S bonds. For the corresponding β-carbonylsulfoxides XC(O)CH$_2$S(O)R[2,5,9,13–15] the *gauche* rotamer is also the more stable, but the *cis* one prevails for some X or R substituents due to electronic[16,17] or steric[17] factors.

In general, the stability of the *gauche* rotamers of β-carbonylsulfides, -sulfoxides and -sulfones has been ascribed to $\pi^*_{CO}/\sigma_{C\text{–}S}$ and $\pi_{CO}/\sigma^*_{C\text{–}S}$ orbital interactions. However, in the case of β-carbonyl-sulfones[10,11] and -sulfoxides,[14,15] additional stabilisation of the *gauche* (or *cis*) rotamer derives from crossed electrostatic and charge transfer interactions between oppositely charged atoms *i.e.* $O_{(SO_2)}\rightarrow C_{(CO)}$ and (or) $O_{(CO)}\rightarrow S_{(SO_n)}$ (n = 1 and 2).

The relevant electronic properties of closely related molecules differing only in the nature of their third row element, such as P or S, are quite similar. In fact, the ionisation energies of the outermost MO (oxygen lone pair) for dimethyl sulfone Me$_2$SO$_2$ (10.65 eV)[18–20] and dimethyl methylphosphonate (MeO)$_2$P(O)Me (10.71 eV)[21] are almost identical. Similarly, the field-inductive parameters for the ethylsulfonyl EtSO$_2$– and diethoxyphosphoryl (EtO)$_2$P(O)– groups are equal ($F \equiv 0.55$).[22] In addition, the attachment energy (*i.e.* the negative of the electron affinity) values for electron capture into the $\sigma^*_{C\text{–}S}$ and $\sigma^*_{C\text{–}P}$ orbitals of Me$_2$S (3.25 eV)[8] and Me$_3$P (3.10)[23,24] are similar, and the $\sigma_{C\text{–}S}$ and $\sigma_{C\text{–}P}$ ionisation energies (12.7[8] and 11.3[25] eV, respectively) are not very different. Therefore, it was interesting to study the α-diethoxyphosphoryl carbonyl compounds (EtO)$_2$P(O)CH$_2$C(O)X (X = Me **1**, Ph **2**, OEt **3**, NEt$_2$ **4** and SEt **5**) by means of IR and ^{13}C NMR spectroscopies and *ab initio* calculations in order to compare these data with those previously reported for the corresponding α-ethylsulfonyl carbonyl compounds[2,9,11] EtSO$_2$CH$_2$C(O)X (X = Me **6**, Ph **7**, OEt **8**, NEt$_2$ **9** and SEt **10**). This paper also reports the X-ray diffraction data and the results of *ab initio* calculations on dialkyl (methylsulfonyl)methylphosphonates (EtO)$_2$P(O)CH$_2$SO$_2$R (R = Et **18**, Me **18a**), necessary to obtain the experimental geometric parameters of the (EtO)$_2$P(O)CH$_2$– group which cannot be easily obtained from the liquid compounds **1**–**5**. Moreover, compound **18** allows a comparison of the relative electron-donor abilities of the sulfonyl and phosphoryl oxygen atoms.

Experimental

Materials

All solvents for IR measurements were spectrograde and were used without further purification. The already known α-diethoxyphosphoryl carbonyl compounds (EtO)$_2$P(O)CH$_2$C(O)X (X = Me **1**,[26] Ph **2**,[27] OEt **3**,[28] NEt$_2$ **4**[28,29] and SEt **5**[30]) were prepared by an adaptation of the method described for **5**, *i.e.*, by reacting equimolar quantities of triethyl phosphite with the corresponding α-bromocarbonyl compound in benzene at room temperature, followed by reflux for 8 hours. The α-diethoxyphosphoryl carbonyl compound was chromatographically separated from isomeric diethyl 1-substituted-vinyl phosphate H$_2$C=C[X][OP(O)(OEt)$_2$] through a silica gel column using hexane–acetone as eluent. After solvent evaporation, the liquid α-diethoxyphosphoryl carbonyl compounds **1**–**5** were

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obtained in a pure form by distillation under reduced pressure. Diethyl (methylsulfonyl)methylphosphonate **18** (mp 92–93 °C, colourless crystals from chloroform) was synthesised following a literature procedure.[31]

IR measurements

The IR spectra were obtained using an FT-IR Nicolet Magna 550 Spectrometer with 1.0 cm^{-1} resolution. For the carbonyl phosphonates **1**–**5** the carbonyl stretching region (1800–1600 cm^{-1}) was recorded in 2.0×10^{-2} mol dm^{-3} carbon tetrachloride, chloroform and acetonitrile solution, using a 0.519 mm sodium chloride cell. The phosphoryl (P=O) stretching region (1300–1100 cm^{-1}) was analysed in carbon tetrachloride solution. The existence of a single symmetric carbonyl stretching band for the series **1**–**5**, in all solvents, was confirmed by Fourier Self Deconvolution (FSD) and second derivative analysis performed on each carbonyl band using the OMNIC Version 1.0 FT-IR software of the Nicolet instrument.

NMR measurements

^1H and ^{13}C NMR spectra of 0.5 mol dm^{-3} solutions in chloroform with TMS as an internal standard were recorded at 200 and 50 MHz, respectively, using a Bruker AC-200 spectrometer in the FT mode. The conditions for recording ^1H and ^{13}C NMR spectra have been described elsewhere.[12]

Calculations

The most stable conformation, the geometric parameters and the electron charge distribution at the various atoms of α-dimethoxyphosphorylacetone **1a**, dimethyl (methylsulfonylmethyl)phosphonate **18a**, α-methylsulfonylacetone **6a**, dimethyl sulfone **19** and dimethyl methylphosphonate **20** were computed at the HF/6-31G** level using the Gaussian 98 series of programs.[32] To save computer time, the ethyl groups were replaced by methyl groups. C_{2v} and C_s symmetry was used for **19** and **20**, respectively, while several (*gauche* and *cis*) starting geometries were used for the other compounds.

Crystal data

$C_6H_{15}O_5PS$, $M = 230.21$, monoclinic, space group $P2_1/a$, $a = 10.074(1)$, $b = 8.3570(9)$, $c = 13.991(2)$ Å, $\beta = 108.46(1)°$, $V = 1117.3(2)$ Å^3, $Z = 4$, $D_x = 1.369$ Mg m^{-3}, λ(Mo-Kα) = 0.71073 Å, $\mu = 0.423$ mm^{-1}, $R = 0.0453$.†

Data collection and processing

X-Ray diffraction data were collected on a CAD4 Mach3 diffractometer with the $\theta/2\theta$ scan technique at 293 K; solution by direct methods (SIR92),[33] full-matrix least-squares refinement on F^2. 2040 measured reflections ($2\theta_{max} = 50°$) yielded 1958 unique and 1463 with $F_o^2 \geq 4\sigma F_o^2$. Anisotropic displacement parameters for all non-H atoms were applied. 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 1.5 (for methyl H atoms) or 1.2 (for the other H atoms) times the value of the equivalent isotropic displacement parameter of the atom to which they are attached. 121 parameters were refined and the final conventional R was 0.0453. Structure refinement, final geometrical calculations were carried out with SHELXL97,[34] PARST-95[35] and WinGX.[36] Fig. 1 was produced using ZORTEP.[37]

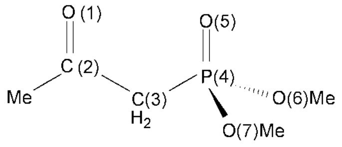
Results and discussion

Table 1 collects the carbonyl stretching frequencies for the α-diethoxyphosphoryl carbonyl compounds **1**–**5**, in carbon tetrachloride, chloroform and acetonitrile. This table also includes the carbonyl stretching frequencies of the predominant *gauche* conformer of the α-ethylsulfonyl carbonyl compounds[2,5,9] **6**–**10** and the corresponding data for the parent

Table 1 Frequencies of the carbonyl stretching bands[a] in the IR spectra of α-diethoxyphosphoryl carbonyl compounds $(EtO)_2P(O)CH_2C(O)X$ **1**–**5**, for the *gauche* conformer[b] of the α-ethylsulfonyl carbonyl compounds $EtSO_2CH_2C(O){-}X$ **6**–**10** and of the parent carbonyl compounds[c] $CH_3C(O){-}X$ **11**–**15**

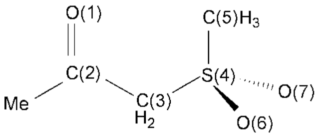
Compound	X	ν/cm^{-1}		
		CCl_4	$CHCl_3$	CH_3CN
1	Me	1719.3	1714.7	1716.1
6[d]		1720.5	1720.0	1723.0
11		1718.5	1711.5	1714.5
2	Ph	1685.0	1681.9	1683.4
7[e]		1680.0	1679.0	1682.0
12		1691.0	1683.0	1693.0
3	OEt	1740.8	1735.0	1736.6
8[f]		1738.0	1739.0	1743.0
13		1742.0	1732.5	1736.6
4	NEt_2	1646.5	1636.8	1637.4
9[f]		1650.0	1644.0	1645.0
14		1650.0	1640.0	1644.0
5	SEt	1687.2	1680.6	1683.7
10[f]		1678.0	1677.5	1681.0
15		1695.0	1687.0	1690.0

[a] Each carbonyl frequency corresponds to the maximum of a single symmetrical band (see Experimental section). [b] The *gauche* conformer is the more abundant one (conc. >80%). [c] From ref. 9. [d,e,f] From refs. 2, 5 and 9, respectively.



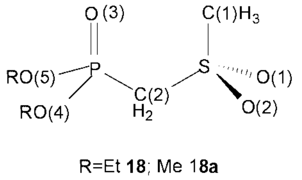
1a

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(7)
γ′ = C(2)-C(3)-P(4)-O(6)



6a

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



R=Et **18**; Me **18a**

α = O(3)-P-C(4)-S
β = P-C(4)-S-C(3)
γ = P-C(4)-S-O(1)
γ′ = P-C(4)-S-O(2)

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† CCDC reference number 188/279. See http://www.rsc.org/suppdata/p2/b0/b005501h/ for crystallographic files in .cif format.

Table 2 Carbonyl frequency shifts ($\Delta\nu_{CO}$)[a] for the α-diethoxyphosphoryl $(EtO)_2P(O)CH_2C(O)$–X **1**–**5** and for the α-ethylsulfonyl $EtSO_2CH_2C(O)$–X **6**–**10** carbonyl compounds, in CCl_4, and the attachment energy values (E_A)[b] for the $\pi^*_{C(O)X}$ orbital of the parent carbonyl compounds $CH_3C(O)$–X **11**–**15**

Compound	X	$\Delta\nu_{CO}$/cm^{-1}	Compound	$\Delta\nu_{CO}$/cm^{-1}	E_A/eV
1–**11**	Me	+0.8	**6**–**11**	+2.0	1.26
2–**12**	Ph	−6.0	**7**–**12**	−11.0	<0[c]
3–**13**	OEt	−1.2	**8**–**13**	−4.0	2.09
4–**14**	NEt_2	−3.5	**9**–**14**	0.0	2.26
5–**15**	SEt	−7.8	**10**–**15**	−17.0	0.95

[a] $\Delta\nu_{CO}$ refers to the difference: $\nu_{\text{substituted carbonyl compound}} - \nu_{\text{parent compound}}$. [b] From ref. 8. [c] The value for acetophenone is not detectable by ETS, from ref. 39.

Table 3 Frequencies of the phosphoryl (ν_{PO}) and sulfonyl asymmetric (ν_{SO_2}) stretching bands in the IR spectra of the α-diethoxyphosphoryl $(EtO)_2P(O)CH_2C(O)$–X **1**–**5** and α-ethylsulfonyl $EtSO_2CH_2C(O)$–X **6**–**10** carbonyl compounds, in CCl_4, and the corresponding frequency shifts ($\Delta\nu$)[a] in relation to the parent compounds **16** and **17**

Compound	X	ν_{PO}/cm^{-1}	$\Delta\nu_{PO}$/cm^{-1}	Compound	$\nu_{SO_2(as)}$/cm^{-1}[b]	$\Delta\nu_{SO_2(as)}$/cm^{-1}
1	Me	1261	+15	**6**	1331	+10
2	Ph	1267	+21	**7**	1332	+11
3	OEt	1270	+24	**8**	1335	+14
4	NEt_2	1253	+7	**9**	1325	+4
5	SEt	1265	+19	**10**	1335	+14
16[c]	—	1246	—	**17**[d]	1321	—

[a] Refers to the difference: $\nu_{\alpha\text{-phosphoryl}}$ or $\nu_{\text{sulfonyl compound}} - \nu_{\text{parent compound}}$. [b] From ref. 9. [c,d] Refers to the parent compounds $(EtO)_2P(O)Me$ and Et_2SO_2, respectively.

Table 4 Carbonyl carbon chemical shifts (δ_C, ppm) in the ^{13}C NMR spectra of the α-diethoxyphosphoryl carbonyl compounds $(EtO)_2P(O)CH_2C(O)$–X **1**–**5**, α-ethylsulfonylcarbonyl compounds $EtSO_2CH_2C(O)$–X **6**–**10** and of the parent carbonyl compounds $CH_3C(O)X$ **11**–**15**, in $CDCl_3$–Me_4Si

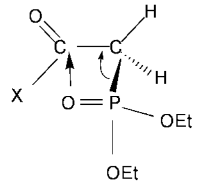
X	Compound	δ_{CO}	Compound	δ_{CO}	$\Delta\delta_{CO}$[a]	Compound	δ_{CO}	$\Delta\delta_{CO}$[a]
Me	**11**	203.7	**1**	200.0	−3.7	**6**	198.0	−5.7
Ph	**12**	196.7	**2**	192.0	−4.7	**7**	189.1	−7.6
OEt	**13**	169.8	**3**	165.8	−4.0	**8**	163.1	−6.7
NEt_2	**14**	164.8	**4**	162.5	−2.3	**9**	161.4	−3.4
SEt	**15**	193.6	**5**	190.4	−3.2	**10**	188.2	−5.4

[a] $\Delta\delta_{CO}$ refers to the difference: $\delta_{\text{substituted carbonyl compound}} - \delta_{\text{reference compound}}$.

carbonyl compounds[9] **11**–**15**. Only a symmetrical carbonyl band is observed for the whole series **1**–**5** in all solvents. The existence of a good linear correlation between the carbonyl frequencies of **6**–**10** and **1**–**5** in carbon tetrachloride [$r = 0.990$; $s = 5.8$ cm^{-1}] suggests that the latter compounds also exist in solution in the *gauche* conformation.[38]

Table 2 lists the carbonyl frequency shifts ($\Delta\nu_{CO}$/cm^{-1}) for **1**–**5** and **6**–**10** in relation to the parent compounds **11**–**15** together with the attachment energy value for the latter compounds. The $\Delta\nu_{CO}$ values for both series are negative, or slightly positive for the methyl derivatives **1** and **6**. The two series are reasonably well correlated ($r = 0.912$) and follow approximately the electron affinity trend of the parent carbonyl compounds[8,39] (except in the case of the methyl derivatives **1** and **6**). These data suggest that the geometry of the α-phosphoryl carbonyl compounds (structure **I**) is similar to that of the *gauche* conformer of the α-sulfonyl carbonyl compounds (structure **II**), whose geometry was previously determined by theoretical calculations and X-ray diffraction analysis. The trends of Table 2 are in line with previous propositions[2,9,12,13] on β-keto sulfones and suggest that the $O_{(PO)}\rightarrow\pi^*_{CO}$ and $O_{(SO_2)}\rightarrow\pi^*_{CO}$ charge transfer and $\pi^*_{CO}/\sigma_{C\text{–}Het}$ hyperconjugative[2,40] interactions are the main factors which stabilise the *gauche* conformation (structures **I** and **II**).

The frequencies of the phosphoryl (ν_{PO}) and asymmetric sulfonyl (ν_{SO_2}) stretching bands of **1**–**5** and **6**–**10** in carbon tetrachloride, and the corresponding frequency shifts with respect to their respective parent compounds **16** and **17** are collected in Table 3. All the frequency shifts are positive and the $\Delta\nu_{SO_2}$ values are *ca.* 1.7 times smaller than the corresponding $\Delta\nu_{PO}$ ones. This behaviour is in line with the absolute carbonyl *gauche* shifts for **6**–**10** being larger than the corresponding values for **1**–**5** (Table 2) and strongly suggests that the $O_{lp}\rightarrow\pi^*_{CO}$ charge transfer interaction in the *gauche* rotamer of β-carbonyl sulfones is stronger than the corresponding interaction for β-carbonyl phosphonates. In fact, a stronger $O_{(SO_2)}\rightarrow\pi^*_{CO}$ charge transfer than the $O_{(PO)}\rightarrow\pi^*_{CO}$ one should lead to a large decrease in the bond order of both C=O and O=S=O oscillators in compounds **6**–**10** and, therefore, in their frequencies, compared to the C=O and P=O oscillators for compounds **1**–**5**.



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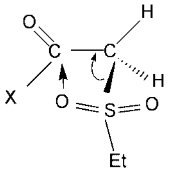


II

Table 4 shows the carbonyl ^{13}C chemical shifts in deuterochloroform for **1**–**5** and **6**–**10** together with the differences ($\Delta\delta$) between the chemical shift of each α-substituted carbonyl compound and the chemical shift of the corresponding parent

Table 5 Relative energy, conformer concentration, dipole moment, selected dihedral angles and interatomic distances of selected non-bonded atoms for the *gauche* (*g*) conformers of $(MeO)_2P(O)CH_2C(O)Me$ **1a** and $MeC(O)CH_2SO_2Me$ **6a**, at the HF/6-31G** level, and the sum of the relevant van der Waals radii

Compound	Conf.[a]	E/kJ mol^{-1}[b]	p (%)[c]	μ/D	Dihedral angles[d]/° α	β	γ	γ'	O(5)···C-(2)/Å[f]	O(1)···P-(4)/Å[g]	O(7)···C-(2)/Å[f]	O(6)···C-(2)/Å[f]
1a	g_1	0.0	87.1	2.28	82.2	45.6	171.6	−81.8	3.128	3.331	3.976	3.416
	g_2	4.78	12.9	2.41	88.2	−165.3	−37.6	68.4	4.057	3.459	3.065	3.234
				μ/D	Dihedral angles[e]/° α	β	γ	γ'	O(6)···C-(2)/Å[f]	O(1)···S-(4)/Å[g]		
6a[h]	g	0.0	>99	3.03	78.8	−70.3	44.9	174.5	2.973	3.298		

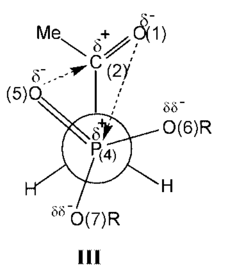
[a] Refers to the *gauche* conformation. [b] Relative energy. [c] Molar fraction of each rotamer as a percentage. [d] α = O(1)–C(2)–C(3)–P(4); β = C(2)–C(3)–P(4)–O(5); γ = C(2)–C(3)–P(4)–O(7); γ' = C(2)–C(3)–P(4)–O(6). [e] α = O(1)–C(2)–C(3)–S(4); β = C(2)–C(3)–S(4)–C(5); γ = C(2)–C(3)–S(4)–O(6); γ' = C(2)–C(3)–S(4)–O(7). [f] Sum of van der Waals radii = 3.22 Å. [g] Sum of van der Waals radii = 3.32 Å. [h] The second minimum energy conformation corresponds to another *gauche* rotamer whose concentration is less than 1%.

Table 6 Charges (*e*) at selected atoms for *gauche* conformers of $MeC(O)CH_2X$: X = $P(O)(OMe)_2$ **1a** and X = SO_2Me **6a** by *ab initio* 6-31G** computations (a minus sign indicates an excess of negative charge)

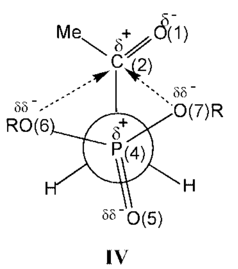
Compound	Conf.	*e*/C $O(5)_{[PO]}$	$O(6)_{[OR]}$	$O(7)_{[OR]}$	$P(4)_{[PO]}$	$C(2)_{[CO]}$	$O(1)_{[CO]}$	$O(6)_{[SO_2]}$	$O(7)_{[SO_2]}$	$S(4)_{[SO_2]}$
1a	g_1	−0.740	−0.718	−0.700	+1.577	+0.498	−0.523			
	g_2	−0.714	−0.716	−0.717	+1.574	+0.512	−0.520			
6a	g					+0.513	−0.514	−0.690	−0.672	+1.457

compound **11–15**. The smaller carbonyl upfield shifts ($\Delta\delta$) of *ca.* 2.0 ppm for the α-phosphoryl derivatives compared to the α-sulfonyl derivatives, in spite of the *quasi* equal field-inductive effect[22] for the diethylphosphoryl and the ethylsulfonyl groups, indicate that the $O_{(PO)}\rightarrow\pi^*_{CO}$ CT interaction in the *gauche* rotamers of series **1–5** is weaker than the $O_{(SO_2)}\rightarrow\pi^*_{CO}$ CT in the corresponding rotamers of series **6–10**, supporting the IR frequency shift analysis.

In order to confirm the *gauche* conformer assignment of the single carbonyl band of the diethoxyphosphoryl carbonyl compounds **1–5**, and to have precise geometries for the *gauche* rotamer of these compounds, *ab initio* calculations on α-dimethoxyphosphorylacetone **1a** (chosen as a representative compound for the whole series) were carried out. The relevant data are presented in Table 5 along with the corresponding data for the *gauche* rotamer of α-methylsulfonylacetone **6a**. The two most stable minima of **1a** have the *gauche* conformation (Structures **III** and **IV**). It seems reasonable, therefore, to decide that the single carbonyl band observed in solution for the whole α-diethoxyphosphoryl carbonyl series **1–5** should correspond to the more abundant g_1 rotamer of **1a** in the gas phase.



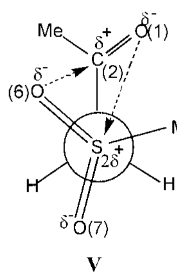
III



IV

The higher stability of the g_1 with respect to the g_2 rotamer is in line with a propitious geometry (structure **III**) giving an intramolecular distance (3.128 Å) between the negatively charged phosphoryl oxygen ($q_O = -0.740$ e) and the positively charged carbonyl carbon ($q_C = +0.498$ e), which is shorter than the sum of the van der Waals radii (3.22 Å) (see Table 5). This close contact produces significant $O^{\delta-}{}_{PO}\rightarrow C^{\delta+}{}_{CO}$ Coulombic and charge transfer interactions. Further stabilisation derives from the distance (3.331 Å) between the carbonyl oxygen ($q_O = -0.523$ e) and the phosphoryl phosphorus ($q_P = +1.577$ e) which is very close to the sum of the van der Waals radii (3.32 Å).

The geometry of the *gauche* conformer of **6a** (see Table 5 and structure **V**) is very close to that of the g_1 conformer of **1a** (structure **III**). However, the O(6)···C(2) and O(1)···S(4) contacts between pairs of oppositely charged atoms are shorter than the corresponding distances for **1a** (g_1) (see Tables 5 and 6). Thus, the HF/6-31G** calculations for **1a** and **6a** corroborate the IR and ^{13}C NMR data for **1–5** and **6–10**, indicating that both series of compounds exist, in the gas phase and in solution, in the *gauche* conformation and that the $O^{\delta-}{}_{SO_2}\rightarrow C^{\delta+}{}_{CO}$ charge transfer and Coulombic interactions in β-carbonyl sulfones are stronger than the $O^{\delta-}{}_{PO}\rightarrow C^{\delta+}{}_{CO}$ CT and Coulombic interactions in β-carbonyl phosphonates.



V

In the less stable g_2 conformer of **1a** the alkoxy oxygens O(6) and O(7) are the donor atoms (structure **IV**). Their interatomic distances from the oppositely charged carbonyl carbon atom C(2) are close to and shorter than, respectively, the sum of the van der Waals radii and shorter than the corresponding distances in the g_1 conformer (see Tables 5 and 6). The lower stability of the g_2 with respect to the g_1 rotamer is probably related to the oxygen lone pair IE values which are higher for the methoxy than for the phosphoryl oxygen (12.0 and

Table 7 Selected dihedral angles and non-bonded distances for the minimum energy conformation of $(MeO)_2P(O)CH_2SO_2Me$ **18a** at the HF/6-31G** level, and the corresponding X-ray data for $(EtO)_2P(O)CH_2SO_2Me$ **18**, and the sum of the relevant van der Waals radii

			Dihedral angles[a]/°						
Compound	Conf.[b]		a	β	γ	γ'	P···O(1)/Å[c]	P···O(2)/Å[c]	S···O(3)/Å[c]
18	*q-g*	X-Ray	−41.8(2)	74.4(2)	−42.5(2)	−170.3(2)	3.180(2)	4.203(2)	3.295(2)
18a	*q-g*	HF/6-31G**	−47.5	69.3	−46.2	−175.5	3.243	4.242	3.417

[a] a = O(3)–P–C(2)–S; β = P–C(2)–S–C(1); γ = P–C(2)–S–O(1); γ' = P–C(2)–S–O(2). [b] Refers to the *quasi-gauche* conformation. [c] Sum of van der Waals radii = 3.32 Å.

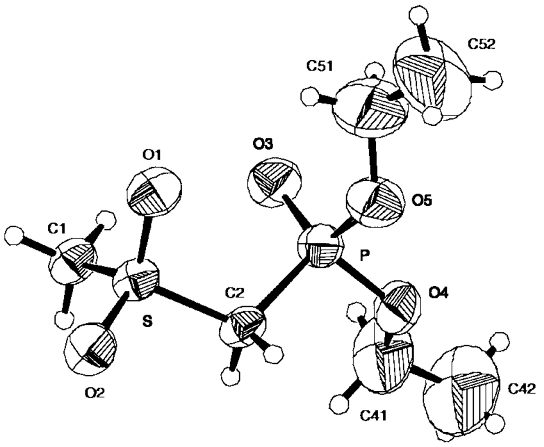


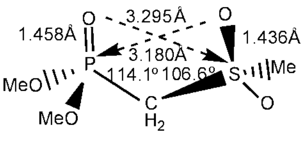
Fig. 1 ZORTEP view of compound **18** showing the thermal ellipsoid at 50% probability and the heavy atom labelling.

10.71 eV, respectively[24] for dimethyl methylphosphonate taken as a reference compound).

The existence of only the g_1 conformer for **1**–**5** in a low permittivity solvent such as carbon tetrachloride (Table 1) can hardly be justified by the small (0.1 D) dipole moment difference between the two *gauche* rotamers of **1a**. However, a close inspection of structures **III** and **IV** shows that the P=O and C=O dipoles are relatively close to each other in g_1 and practically directly opposite each other in g_2. Therefore, even the low relative permittivity but polarizable nature of carbon tetrachloride as solvent would stabilise the g_1 to a greater extent than the g_2 conformer.

Direct information about the relative donor/acceptor ability of the PO and SO_2 groups has been obtained from an X-ray single crystal analysis of diethyl (methylsulfonyl)methyl phosphonate **18**. Fig. 1 and Table 7 show that in the solid state **18** assumes a *syn-clinal* or *quasi-gauche* geometry with respect to both the a (−41.8°) and γ (−42.5°) dihedral angles. Moreover, the O(1) ··· P contact (3.18 Å) is significantly shorter than the sum of the relevant van der Waals radii (3.32 Å), while the O(3) ··· S contact (3.295 Å) is only slightly smaller. The most stable conformer of **18a** from HF/6-31G** calculations has practically the same geometrical parameters as those obtained by X-ray diffraction for **18**. In conclusion, this model compound shows that the $O_{(SO_2)}\rightarrow P_{(PO)}$ charge transfer interaction between the sulfonyl oxygen ($q_O = -0.700$ e) and the phosphoryl phosphorus ($q_P = 1.601$ e) occurs over a shorter distance and is likely to be more pronounced than the interaction between the phosphoryl oxygen ($q_O = -0.743$ e) and the sulfonyl sulfur ($q_s = 1.459$ e), giving some support to the fact that $O_{(SO_2)}$ in **6**–**10** is a better electron donor toward the π^*_{CO} orbital than $O_{(PO)}$ in **1**–**5**.

The better electron-donor ability of the sulfonyl oxygen lone pair $n_{O(SO_2)}$ than the phosphoryl oxygen lone pair $n_{O(PO)}$ towards the π^*_{CO} orbital would appear to be unexpected. In fact, the basicity of the oxygen atom of the phosphoryl group evaluated from the ν_{OH} frequency shift in the diethyl ethylphosphonate–phenol complex with respect to phenol (CCl_4, $\Delta\nu_{OH} = 398$ cm^{-1})[41] is more than twice the basicity of the oxygen of the sulfonyl group estimated for the dimethyl sulfone–*p*-fluorophenol complex ($\Delta\nu_{OH} = 154$ cm^{-1}),[42] and the basicity trend is in line with the larger negative charge at $O_{(PO)}$ in **19** (−0.743 e) than at $O_{(SO_2)}$ in **20** (−0.678 e). However, in the model compound **18/18a** (structure **VI**), the CH_2–S=O angle and the S=O bond length are smaller, respectively, than the CH_2–P=O angle and the P=O bond length. Moreover, the corresponding parameters O=P–CH_3 (118.0°) and the P=O (1.459 Å) for $MeP(O)(OMe)_2$ **19**, and O=S–CH_3 (107.8°) and S=O (1.435 Å) for Me_2SO_2 **20** are very close to those computed for **18a**. Thus, these intrinsic geometrical parameters, which allow close contact between oppositely charged atoms in **18**, seem to be responsible for the abnormally stronger electron-donor ability of the sulfonyl oxygen lone pair $n_{O(SO_2)}$ in **6**–**10** than the phosphoryl oxygen lone pair in **1**–**5**.



VI

Conclusions

The IR frequency of the single ν_{CO} band of the β-carbonylphosphonates $[XC(O)CH_2P(O)(OEt)_2$: X = Me **1**, Ph **2**, OEt **3**, NEt_2 **4** and SEt **5**] (series **I**), which correlates well with the ν_{CO} frequencies of the *gauche* rotamer of the corresponding β-carbonyl sulfones $[XC(O)CH_2SO_2Et$: X = Me **6**, Ph **7**, OEt **8**, NEt_2 **9** and SEt **10**] (series **II**) along with *ab initio* 6-31G** computations for **1a** and **6a** (X = Me) indicate the existence of a single *gauche* conformer (g_1) for series **I** in solution.

The abnormal negative carbonyl frequency shifts ($\Delta\nu_{CO}$) for both series approximately follow the electron affinities of the π^*_{CO} orbital of the parent carbonyl compounds MeC(O)X **11**–**15**. These data suggest that the *gauche* conformations of series **I** and **II** should have similar geometries.

The less positive asymmetric sulfonyl frequency shifts ($\Delta\nu_{SO_2}$) in comparison with the phosphoryl frequency shifts ($\Delta\nu_{PO}$) and the larger negative carbonyl *gauche* conformer shifts of β-carbonyl sulfones **6**–**10** in relation to the corresponding values of the β-carbonyl phosphonates **1**–**5** are in line with the greater upfield carbonyl ^{13}C chemical shifts for series **II** with respect to series **I**. These trends are in agreement with their $O_{(SO_2)} \cdots C_{(CO)}$ distances which are shorter than $O_{(PO)} \cdots C_{(CO)}$ in compounds **6a** and **1a**, respectively, and are discussed in terms of the $O_{lp}\rightarrow\pi^*_{CO}$ charge transfer and electrostatic interactions, which are stronger for series **II** than for **I**. This unexpected behaviour indicates that the sulfonyl oxygen atom of the SO_2R group is a better electron donor than the phosphoryl oxygen atom of the $P(O)(OR)_2$ group. The intrinsic geometric parameters of the

O=S–CH_2 and O=P–CH_2 moieties seem to be responsible for this behaviour. In fact, X-ray and *ab initio* calculations of dialkyl (methylsulfonyl)methylphosphonate $MeSO_2CH_2P(O)(OR)_2$ (R = Et, **18**, Me **18a**) support this analysis.

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