Spectroscopic and theoretical studies on the conformation of some α-sulfinylacetophenones

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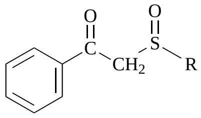
IR ν_{CO} and ν_{SO} frequencies of some α-sulfinylacetophenones [$PhC(O)CH_2S(O)R$: R = Me 1, Et 2, Pr^i 3, Ph 4 and Bu^t 5] have been measured and their conformations are estimated with the help of *ab initio* 6-31G calculations and X-ray diffraction analyses. The anomalous negative carbonyl frequency shifts for the *cis*$_2$ rotamer together with the decrease of the *cis*:*gauche* population ratio in solvents of increasing polarity for compounds 1–4 support the existence of a strong intramolecular interaction between C=O and S=O dipoles, which stabilizes the *cis*$_2$ rotamer more than the π_{CO}–σ^*_{C-SO} and π^*_{CO}–σ_{C-SO} orbital interactions stabilize the *gauche*$_3$ rotamer. The stability of the *cis*$_2$ rotamer is discussed in terms of the electrostatic attraction between the C=O and S=O dipoles along with the $\pi^*_{S=O}\leftarrow n_{O(CO)}$ charge transfer which lead to an $O_{(CO)}\cdots S_{(SO)}$ contact shorter than the sum of the corresponding van der Waals radii. The *gauche*$_2$ rotamer of 5 is more stable than the *cis*$_2$ one in which steric strain between the carbonyl oxygen atom and the *tert*-butyl group is present.**

Our previous studies on some β-keto sulfides and β-keto sulfones $RC(O)CH_2SO_nR'$ [1–8] (R = methyl, aryl; R′ = alkyl, aryl; $n = 0, 2$) by IR, ^{13}C NMR, UV–VIS and UPS spectroscopies and X-ray diffraction (for the β-keto sulfones), supported by molecular mechanics, semi-empirical and *ab initio* calculations, indicated that these compounds in the gas phase, in solution and in the solid state prefer the *gauche* conformation.

In general the stability of the *gauche* rotamers of the β-keto sulfides, β-keto sulfoxides and β-keto sulfones has been ascribed to the π^*_{CO}–σ_{C-S} and π_{CO}–σ^*_{C-S} orbital interactions.[1] However, in the case of the β-keto sulfones[7,8] an additional stabilization of the *gauche* rotamer occurs, due to electrostatic and crossed charge transfer interactions between the sulfonyl oxygen and the carbonyl carbon atoms and between the carbonyl oxygen and the sulfonyl sulfur atoms.

For the β-keto sulfoxides $RC(O)CH_2S(O)R'$ the *gauche* rotamer is also more stable for the acetone derivatives[1,9] (R = methyl; R′ = alkyl, aryl) but the *cis* rotamer is more stable for some acetophenone derivatives (R = phenyl; R′ = methyl, phenyl). Our recent study on α-methylsulfinylacetophenone[10] by X-ray diffraction, UV photoelectron spectroscopy and *ab initio* 6-31G** calculations along with the IR results for the methylsulfinyl- and phenylsulfinyl-acetophenones[11,12] have indicated that the CH_2–S(O) bond is quasi-*cis* to the carbonyl group in the gas and solid phases and in solution, and that the *cis* conformation is stabilized by electrostatic and charge transfer interactions, between the negatively charged carbonyl oxygen atom and the positively charged sulfur atom.

In order to further investigate the stability of the *cis* rotamer of the acetophenone sulfoxides, this paper reports on α-sulfinylacetophenones $PhC(O)CH_2S(O)R$, with the sulfinyl group substituent of increasing size, *i.e.* R = methyl **1**, ethyl **2**, isopropyl **3**, *tert*-butyl **5** and phenyl **4**, by means of IR spectroscopy, X-ray diffraction and *ab initio* calculations.



1 R = Me
2 R = Et
3 R = Pr^i
4 R = Ph
5 R = Bu^t

Experimental

Materials

The (spectrograde) solvents for IR measurements were used without further purification. α-Methylsulfinyl-, **1**,[13] ethylsulfinyl-, **2**,[14] phenylsulfinyl-, **4**[15] and *tert*-butylsulfinyl-, **5**[16] acetophenones were prepared by literature procedures. α-Isopropylsulfinylacetophenone, **3**, is a new compound and was obtained by the oxidation of the α-(isopropylthio)acetophenone with an equivalent amount of 30% hydrogen peroxide dissolved in acetic acid at 0 °C over 10 h. After the reaction work-up, 82% yield of the pure colourless oil was obtained from a silica gel chromatographic column using hexane–acetone as eluent: δ_H($CDCl_3$) 1.33 [d, 3H, *J* 6.6, $CH(CH_3)_2$], 1.34 [d, 3H, *J* 6.6, $CH(CH_3)_2$], 2.68–3.08 [septet, 1H, *J* 6.6, $CH(CH_3)_2$], 4.22 (d, 1H, *J* 14, CH_2), 4.34 (d, 1H, *J* 14, CH_2), 7.44–7.65 (m, 3H, Ar*H*), 7.98 (d, 2H, Ar*H*) (Found: C, 62.70; H, 6.76. Calc. for $C_{12}H_{16}O_2S$: C, 62.83; H, 6.71%). The α-(*tert*-butylthio)acetophenone is a new compound and was obtained in 61% yield, following a literature procedure.[17] Bp 92–93 °C (0.15 Torr); δ_H($CDCl_3$) 1.34 [s, 9H, $C(CH_3)_3$], 3.82 (s, 2H, CH_2), 7.79–7.50 (m, 3H, Ar*H*), 7.92–7.95 (m, 2H, Ar*H*) (Found: C, 69.27; H, 7.77. Calc. for $C_{12}H_{16}O_2S$: C, 69.19; H, 7.74%).

IR measurements

The IR spectra were obtained on an FTIR Nicolet Magna 550

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Table 1 Frequencies and intensities of the carbonyl stretching bands in the IR spectra of α-sulfinylacetophenones $PhC(O)CH_2S(O)R$ **1**–**5** and the frequencies of acetophenone **6**

		n-C_6H_{14}		CCl_4				$CHCl_3$		CH_3CN		DMSO		Solid
Comp.	R	ν/cm^{-1}	α_c/α_g[a,b]	ν/cm^{-1}	α_c/α_g	ν/cm^{-1}[c]	α_c/α_g	ν/cm^{-1}	α_c/α_g	ν/cm^{-1}	α_c/α_g	ν/cm^{-1}	α_c/α_g	ν/cm^{-1}
1	Me	1683.0	1.63	1680.0	2.00	3344.0	1.20	1678.5	2.31	1686.0	0.58	1680.5	0.89	1674.5[d]
		1675.0		1671.0		3329.0		1670.0		1678.0		1671.0		—
2	Et	1682.9	2.00	1678.7	3.18	3338.2	6.00	1676.5	4.43	1685.5	0.86	1670.1	2.57	1682.9[d]
		1673.9		1669.8		3320.9		1667.8		1677.6		1638.2		—
3	Pr^i	1682.2	3.00	1678.4	3.82	3338.5	7.00	1677.1	3.22	1686.0	1.18	1677.6	2.42	—[e]
		1673.1		1669.1		3322.0		1668.3		1677.1		1661.2		
4	Ph	1685.0	—	1682.0	30.0	3346.0	9.00	1681.0	1.90	1686.0	0.94	1691.0	1.70	1670.0[d]
		—		1676.0		3329.0		1675.0		1683.0		1684.0		—
5	Bu^t	1692.4	0.20[h]	1686.6	0.24	3358.1	0.38	1684.3	0.65	1686.7	1.72	1676.2	3.25	1684.0[d]
		1684.4[f]	—	1679.2		3339.5		1676.2		1678.8		1645.6		—
		1672.6[g]	0.13[h]	—		—		—		—		—		
6[i]	—	1696.0		1691.0	—	3362.5	—	1683.0	—	1686.0	—	1681.9	—	—

[a] Ratio of the absorbances of the high and low frequency components of the analytically resolved doublet. [b] Subscripts *c* and *g* indicate *cis* and *gauche* rotamers. [c] First overtone. [d] Single symmetrical band. [e] Compound **3** is a liquid. [f,g] Refers to two *gauche* rotamers. [h] Ratios of the absorbances of the highest and the lowest triplet frequency components in relation to the absorbance of the more intense middle frequency component. [i] Acetophenone.

spectrometer, with 1.0 cm^{-1} resolution. The carbonyl stretching region (1800–1600 cm^{-1}) was recorded in 3.0 × 10^{-2} mol dm^{-3} carbon tetrachloride, chloroform, acetonitrile and dimethyl sulfoxide solutions and in a *ca.* 10^{-3} mol dm^{-3} *n*-hexane solution, using a 0.519 mm sodium chloride cell. For the carbonyl first overtone region (3600–3100 cm^{-1}) the spectra were obtained in 3.0 × 10^{-2} mol dm^{-3} carbon tetrachloride solution using 1.00 cm quartz cell. The carbonyl band for solids **1**, **2**, **4** and **5** was obtained in KBr pellets. The sulfinyl stretching region (1100–1000 cm^{-1}) was recorded in carbon tetrachloride solutions under the same conditions as described above (see Table 1).

The overlapped carbonyl stretching bands were deconvoluted by a curve fitting program based on the unrestricted Cauchy–Gauss sum function.[18,19] Minor modifications were introduced[20] by using the half band width and the Cauchy–Gauss shape ratio as input parameters. The non-linear baseline was optimized[20] by the introduction of an additional component having a Gaussian profile and a very large half-width.

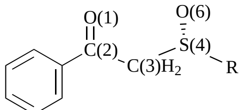
The relative concentrations of the *cis–gauche* rotamers for **1**–**5** were estimated[21] from the absorbance ratio at the maxima (α_c/α_g) of the carbonyl band components, assuming equal molar absorptivity coefficients for the various rotamers.

NMR measurements

^1H NMR spectra were recorded at 200 MHz on a Bruker AC-200 spectrometer in deuteriochloroform using TMS as an internal standard, *J* values are given in Hz.

Calculations

The geometric parameters and the electron charge distribution at the various atoms of *tert*-butylsulfinyl- and ethylsulfinylacetophenone were computed at the *ab initio* level using the GAUSSIAN92 series of programs.[22] To determine the preferred conformation of **2** and **5** we optimized at the HF/6-31G** level (*d* functions on S, C and O and *p* functions on H) four starting conformations corresponding to the two lowermost *cis* and the two lowermost *trans* conformations previously[10] obtained for the corresponding methyl derivative, **1**. The dihedral angles α, β and γ are defined below ($\alpha = 0°$: *cis* conformation). Complete relaxation of all the internal parameters was allowed for the ethyl derivative, while for **5**, the C–H bond distances of the *tert*-butyl group were kept equal in a conformer, and the HCC bond angles, equal in a methyl group, were allowed to change for different groups. These restrictions provided C–H bond distances (1.0842–1.0847 Å) and HCC angle (110.5–111.2°) values close to those fully optimized for the various conformers of **2** (1.0836–1.0846 Å and 110.5–110.6°, respectively).



α = O(1)-C(2)-C(3)-S(4)
β = C(2)-C(3)-S(4)-R
γ = C(2)-C(3)-S(4)-O(6)

Crystal data

Only low quality hygroscopic crystals were obtained after many attempts by diffusion methods from chloroform–*n*-hexane solutions.†

$C_{10}H_{12}O_2S$, (**2**) $M = 196.27$, monoclinic, space group $P2_1/a$, $a = 10.330(2)$, $b = 12.974(4)$, $c = 15.704(6)$ Å, $\beta = 106.31(3)°$, $V = 2020(1)$ Å^3, $Z = 8$, $D_x = 1.29$ mg m^{-3}, λ(Mo-Kα) = 0.710 69 Å, $R = 0.146$.

$C_{12}H_{16}O_2S$, (**5**) $M = 224.32$, monoclinic, space group $P2_1/n$, $a = 5.852(1)$, $b = 11.524(4)$, $c = 18.804(3)$ Å, $\beta = 90.95(2)°$, $V = 1267.9(5)$ Å^3, $Z = 4$, $D_x = 1.18$ mg m^{-3}, λ(Mo-Kα) = 0.710 69 Å, $R = 0.121$.

Data collection and processing

X-Ray diffraction data were recorded on a CAD4 diffractometer with $\omega/2\theta$ scan technique, graphite monochromated Mo-Kα radiation ($\lambda = 0.710$ 69 Å), $T = 295$ K. Solution by direct methods (SIR 92).[23] Full matrix least-squares refinement. For **2** the 4527 measured reflections ($2\theta_{max} = 52°$) yielded 4098 unique and 1398 reflections with $F_o^2 \geqslant 4\sigma F_o^2$. Anisotropic thermal parameters for all non-hydrogen atoms were applied and two unique isotropic thermal parameters ($U = 0.05$ Å^2 for non-methyl and $U = 0.07$ Å^2 for methyl hydrogens) were assigned to the hydrogen atoms introduced in the calculated positions. 265 parameters were refined (mean $\delta/\sigma = 0.02$) and the final conventional *R* was 0.146 [$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$]. (The average esd of a C–C bond was 0.02 Å.) For **5** the 1568 measured reflections ($2\theta_{max} = 42°$) yielded 1310 unique and 630 reflections with $F_o^2 \geqslant 4\sigma F_o^2$. Anisotropy was applied only to the non-phenyl atoms which were refined as isotropic rigid groups and to the non-methyl groups. The H-atoms were introduced in calculated positions with isotropic thermal parameters 20% higher than the attached carbon. 88 parameters were refined and the

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† Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 2*, available *via* the RSC Web pages (http://chemistry.rsc.org/rsc/p1pifa.htm). Any request to the CCDC for this material should quote the full literature citation and the reference number 188/108.

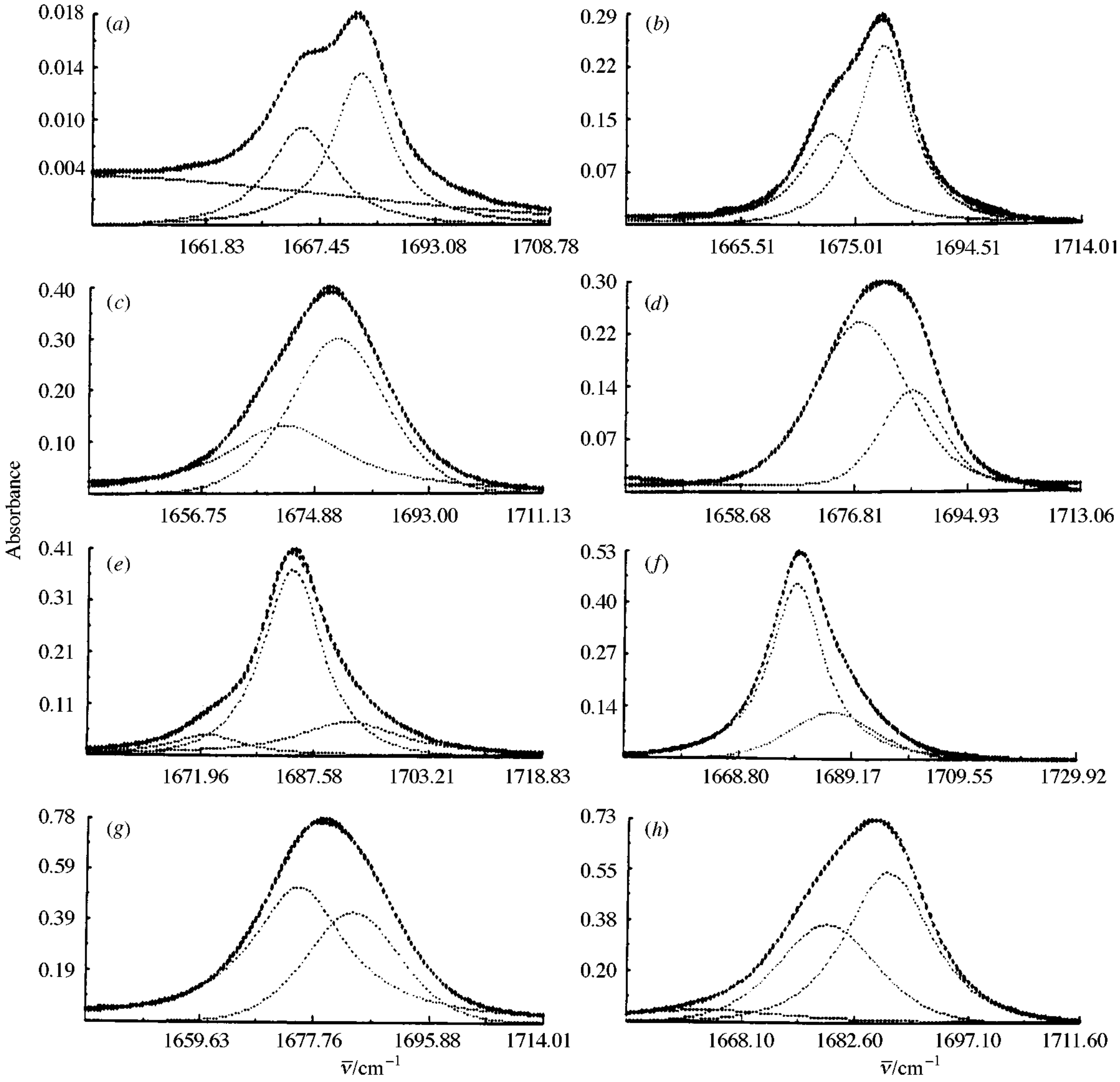


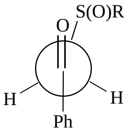
Fig. 1 IR analytically resolved carbonyl stretching bands of the α-methylsulfinylacetophenone **1** and of α-*tert*-butylsulfinylacetophenone **5**: in *n*-hexane (*a*), (*e*); carbon tetrachloride (*b*), (*f*); chloroform (*c*), (*g*); and acetonitrile (*d*), (*h*), respectively

final conventional R was 0.121 [$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$]. Structure refinement and final geometrical calculations were carried out with SHELXL-93[24] and PARST[25] programs. Drawings were produced using ORTEP II.[26]

Results and discussion

Table 1 collects the stretching frequencies and the absorbance ratios of the analytically resolved carbonyl bands for the α-alkylsulfinyl- (**1**–**3**, **5**) and α-phenylsulfinyl- (**4**) acetophenones in *n*-hexane, carbon tetrachloride (fundamental and first overtone), chloroform, acetonitrile, dimethyl sulfoxide and in the solid state. The frequencies of the parent acetophenone **6** are included for comparison. Compounds **1**–**5** show in all solvents a doublet, except in *n*-hexane where **4** and **5** have a single symmetrical band and a triplet, respectively. The intensity ratio of the components of the doublet for compounds **1**–**4** varies slightly in solvents of low relative permittivity[27] (*n*-hexane, $\varepsilon = 1.9$; carbon tetrachloride, $\varepsilon = 2.2$; and chloroform, $\varepsilon = 4.8$), where the higher frequency component is the more intense. However, in high relative permittivity solvents (acetonitrile, $\varepsilon = 38$; and dimethyl sulfoxide, $\varepsilon = 47$) there is a significant increase of the lower frequency component. For compound **5** the lower frequency component is more intense in solvents of low polarity and less intense in solvents of high polarity.

The solvent effect on the carbonyl band components for **1**, as a prototype for compounds **1**–**4**, and **5** is illustrated in Fig. 1. The behaviour of **5** shows the presence of conformational isomerism,[28a] while an anomalous solvent effect is observed for **1**. However, the occurrence of two carbonyl bands in the first overtone region at frequencies approximately twice those in the fundamental region and of about the same intensity ratios is evidence of *cis*–*gauche* rotational isomerism[29] for the whole series **1**–**5**. As outlined below, it seems reasonable to attribute the higher frequency component of the doublet to the more polar *cis* rotamer (structure **I**) and the lower one to the less polar *gauche* rotamer (structure **II**). In addition, the single carbonyl band (**4**) and the lowest frequency component of the triplet (for **5**) observed in *n*-hexane correspond to the *cis* and a second *gauche* rotamer, respectively.



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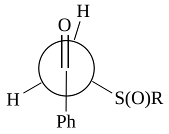


II

The X-ray molecular structures of **2** and **5** are shown in Fig. 2. The dihedral angles *α*, *β* and *γ* are listed in Table 2, together

Table 2 Relative energy, dipole moments and selected dihedral angles optimized for different *cis* (*c*) and *gauche* (*g*) conformers of some PhC(O)CH$_2$S(O)R at the 6-31G** level and corresponding X-ray geometrical data, and the sum of the relevant van der Waals radii

Comp.	R			Relative energy/ kJ mol^{-1}	P^a (%)	μ/D	Dihedral angles/°^{b} α	β	γ	C(2)···O(6)/Å^c	O(1)···S(4)/Å^d
1	Me^e	X-Ray (c_1)					−8.8(7)	−178.7(5)	−71.0(4)	3.246(7)	2.874(5)
		6-31G**	c_1:	12.41	0.4	6.44	−15.7	172.4	−78.9	3.304	2.873
			c_2:	0.00	63.1	5.37	8.2	−72.2	178.5	3.972	2.940
			g_1:	7.18	3.5	3.83	88.8	−76.4	173.4	3.980	3.416
			g_2:	5.60	6.6	3.16	88.7	−166.5	84.4	3.409	3.403
			g_3:	2.17	26.3	2.08	88.8	−51.5	60.2	3.265	3.481
2	Et	X-Ray (**I**) (c_1)					−1(3)	177(2)	−71(2)	3.31(3)	2.86(4)
		X-Ray (**II**) (c_1)					−6(3)	177(2)	−74(2)	3.22(4)	2.81(2)
		6-31G**	c_1:	11.77	0.6	6.31	−15.2	171.5	−79.7	3.315	2.877
			c_2:	0.00	62.1	5.18	7.9	−73.2	177.5	3.974	2.943
			g_2:	4.44	10.5	3.07	89.7	−164.59	86.2	3.429	3.413
			g_3:	2.08	26.8	1.80	89.6	−51.7	60.6	3.274	3.495
5	Bu^t	X-Ray (c_1)					−8(2)	171(1)	−75(1)	3.28(2)	2.79(2)
		6-31G**	c_1:	8.44	2.6	6.15	−15.7	169.2	−81.2	3.293	2.870
			c_2:	5.79	7.6	5.02	8.3	−93.6	156.8	3.941	2.970
			g_2:	0.00	77.2	2.98	90.2	−159.1	90.7	3.435	3.399
			g_3:	3.87	12.6	1.08	100.5	−50.8	63.4	3.405	3.668

[a] Molar fraction of each rotamer in percentage. [b] α = O(1)–C(2)–C(3)–S; β = C(2)–C(3)–S–R; γ = C(2)–C(3)–S–O. [c] Sum of van der Waals radii = 3.22 Å. [d] Sum of the van der Waals radii = 3.32 Å. [e] From ref. 10.

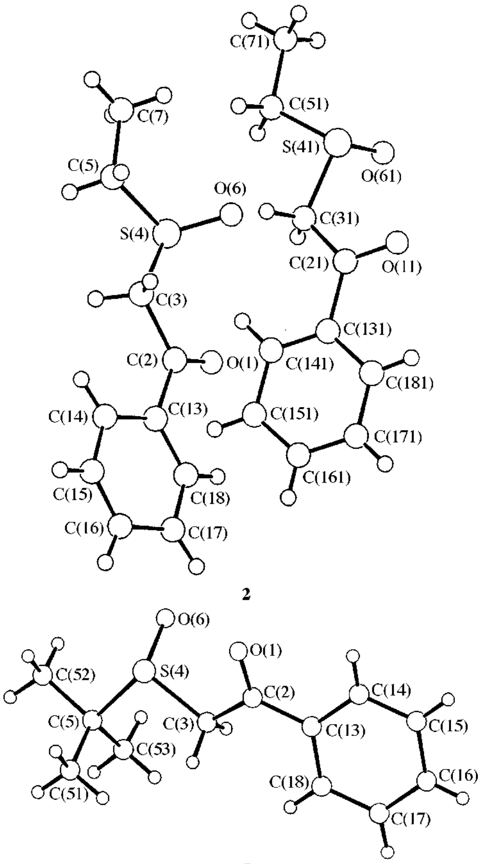
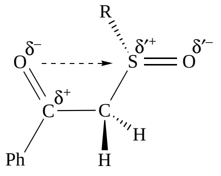


Fig. 2 X-Ray crystal structures of compounds **2** and **5** with heavy atoms labelling. The size of the atoms is arbitrary. For **2** the two independent molecules present in the unit cell are reported.

with the values obtained by fully optimized *ab initio* 6-31G** calculations for the c_1, c_2, g_2 and g_3 conformations, and with the corresponding data for **1**.[10] The C(2)···O(6) and O(1)···S(4) non-bonded interatomic distances are also reported. The predicted distribution of the two more stable conformers *cis*$_2$ (*ca.* 60%) and *gauche*$_3$ (*ca.* 30%) of **1** and **2** is very close to that obtained from the intensity ratios of the high and low frequency carbonyl doublet components in *n*-hexane (Table 1; 65% and 35%, respectively). Therefore, it may be assumed that the high and low frequency components of the carbonyl doublet correspond to the *cis*$_2$ and *gauche*$_3$ conformers, respectively, not only for **1** and **2** but also for **3** and **4**. This assignment is supported by the frequencies of each carbonyl doublet component in all solvents, and also by the similar solvent effect on the relative intensities of the carbonyl doublet as described above (see Table 1).

For compound **5** (Table 2) the *gauche*$_2$ conformer is the most stable (*ca.* 77%, HF/6-31G**) in agreement with the very intense middle component of the carbonyl triplet in *n*-hexane (*ca.* 75%, Table 1). The second and third stable conformers are the *gauche*$_3$ and *cis*$_2$ (13 and 8%, respectively). Although the highest frequency component of the carbonyl triplet in *n*-hexane is slightly more intense than the lowest component (see Fig. 1), the former may be ascribed to the more polar *cis*$_2$ rotamer (μ = 5.02 D) and the latter to the less polar *gauche*$_3$ rotamer (μ = 1.08 D) in agreement with the disappearance of the lowest frequency triplet component in polar solvents.

The most polar and least stable *cis*$_1$ rotamers for **1**, **2** and **5** obtained by *ab initio* calculations have about the same geometry of the crystals and are the only rotamers present in solid state (Fig. 2), in agreement with the single carbonyl band observed in the IR spectra (Table 1). The molecular structures have α dihedral angles close to that of the *cis*$_2$ rotamers (Table 2). However, the β and γ values are interchanged with respect to those of the *cis*$_2$ rotamers. Thus, in the *cis*$_1$ rotamers the angle between the C=O and S=O dipoles is small (Table 2) leading to a large repulsive field effect[28b] between them. This agrees with the decrease of the negative charge at the carbonyl and sulfinyl oxygen atoms in the *cis*$_1$ in comparison with the *cis*$_2$ rotamers (Table 3). Both *cis*$_1$ and *cis*$_2$ rotamers possess high dipole moments (*ca.* 6.30 and 5.20 D, respectively), and the stabilization of the *cis*$_1$ over the *cis*$_2$ form in the crystals may be associated with a larger energy gain deriving from dipole moment coupling. Therefore, it can be concluded from the X-ray analysis and *ab initio* calculation for the β-keto sulfoxides **1**, **2** and **5** together with the IR data for the whole series, that the *cis*$_1$ conformation is preferred in the solid state for **1**–**5**. In the gas phase and in solvents of low polarity, the *cis*$_2$ and *gauche*$_2$ conformations prevail for **1**–**4** and **5**, respectively. The higher stability of the polar *cis*$_2$ rotamer for **1**–**4** agrees with its geometry (structure **III**) which allows short-range intramolecular contact between the carbonyl oxygen and the sulfur atom. In fact, in **1** and **2** the carbonyl oxygen has a negative charge (*ca.* −0.52 e) and is separated from the sulfur, positively charged (*ca.* +1.03 e), by a distance of about 2.9 Å, shorter than the sum of the van der Waals radii (3.32 Å) (Table 2).



III

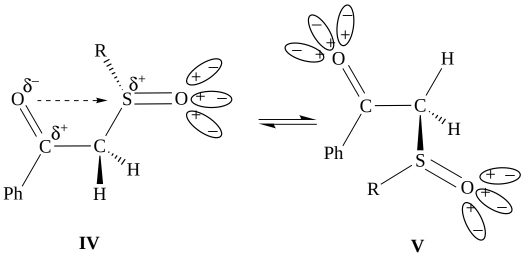
The carbonyl frequency shifts with respect to the parent compound **6** ($\Delta\nu$) in *n*-hexane, carbon tetrachloride and chloroform, for the *cis* and *gauche* rotamers of the β-keto sulfoxides **1**–**5**, are listed in Table 4. Both the *cis* ($\Delta\nu_c$) and *gauche* ($\Delta\nu_g$) shifts are negative, the latter being, in general, much larger than the *cis* ones. The *cis* shifts for **1**–**5** refer to the *cis*$_2$ rotamers. The *gauche* shifts for **1**–**4** and the more negative one for **5** in *n*-hexane correspond to the *gauche*$_3$ rotamers, whilst the remaining $\Delta\nu_g$ value for **5** corresponds to the *gauche*$_2$ rotamer as shown below.

The significant negative *gauche* shifts agree with the prevalence of the π_{CO}–$\sigma^*_{C\text{–}SO}$ orbital interactions over the −I effect of the alkylsulfinyl or phenylsulfinyl groups [$\sigma_{I(S(O)R,\ S(O)Ph} \cong 0.50$],[30] leading to a decrease in the carbonyl force constant and, therefore, in the ν_{CO} frequencies with respect to the parent acetophenone **6**.

On the other hand, the anomalous approximately constant negative *cis* shifts (Table 4) along with the unexpected decrease of the population of the more polar *cis* rotamer in solvents of high polarity for **1**–**4** (Table 1) support the existence of a strong intramolecular interaction between the carbonyl oxygen and the sulfur atoms (see structure **IV**) responsible for the decrease in the carbonyl frequencies. Moreover, the *cis*–*gauche* equilibrium is shifted towards the less polar *gauche* form only in solvents of high polarity, because in conformation **V** the C=O dipole is further away from the sulfinyl sulfur. This geometry allows a better solvation of the oxygen atom of the C=O dipole, as the oxygen atom of the S=O dipole seems to be solvated by approximately the same amount in both rotamers.

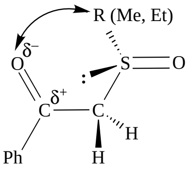
Table 3 Charges at selected atoms (*e*) for compounds **1**, **2** and **5**, PhC(O)CH$_2$S(O)R obtained by *ab initio* 6-31G** computations (a minus sign indicates an excess of negative charge)

Comp.	R	Conformer	*e*/C C$_{(CO)}$	O$_{(CO)}$	S$_{(SO)}$	O$_{(SO)}$
1	Me	c_1	0.553	−0.523	1.018	−0.785
		c_2	0.540	−0.545	1.004	−0.798
		g_1	0.521	−0.537	0.964	−0.783
		g_2	0.526	−0.528	0.984	−0.789
		g_3	0.549	−0.542	0.963	−0.787
2	Et	c_1	0.552	−0.523	1.031	−0.793
		c_2	0.541	−0.545	1.018	−0.806
		g_2	0.526	−0.530	1.000	−0.797
		g_3	0.549	−0.542	0.975	−0.795
5	Bu^t	c_1	0.553	−0.523	1.050	−0.809
		c_2	0.543	−0.537	1.044	−0.821
		g_2	0.524	−0.532	1.015	−0.814
		g_3	0.569	−0.552	0.990	−0.802

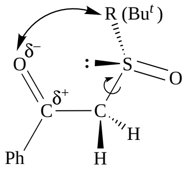


IV **V**

The $\Delta\nu$ values for compound **5** agree with the peculiar relative stabilities of its rotamers. The larger steric hindrance[31] between the R and the carbonyl group in the *cis*$_2$ rotamer of **5** with respect to **1**–**4** causes a rotation of the sulfinyl group of about 20° around the C(3)–S bond (see Table 2 and structures **VI** and **VII**). As a consequence, the O(1)···S distance increases (by about 0.03 Å), decreasing the stabilizing charge transfer and electrostatic interactions, and then *cis*$_2$ is no longer the most stable conformer. The rotation of the sulfinyl group also increases the repulsive field effect between the negatively charged carbonyl oxygen and the sulfur lone pair[32] causing a slight decrease of the negative charge at O(1) and an increase in the carbonyl frequency, in agreement with the smaller $\Delta\nu_c$ value for the *cis*$_2$ rotamer of **5**.



VI



VII

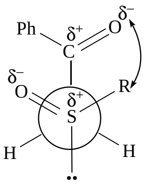
In addition, there is a closer proximity between the carbonyl oxygen and the alkyl group in structure **VIII** (*gauche*$_3$) than in **IX** (*gauche*$_2$). The bulky Bu^t group, therefore, perturbs the *gauche*$_3$ geometry ($\Delta\alpha \approx 10°$) more than the *gauche*$_2$ one ($\Delta\gamma \approx 5°$) compared to the less hindered derivatives (see Table 2). So, *gauche*$_2$ is the most stable conformer for **5**, explaining its peculiar $\Delta\nu_g$ value in all solvents.

The higher carbonyl frequency in the *gauche*$_2$ than in the *gauche*$_3$ rotamer for **5** can be explained by the smaller electrostatic attraction between C(2) and O(6) and also by the larger repulsive field effect between the sulfur lone pair and the negatively charged carbonyl oxygen (see Tables 3 and 4).

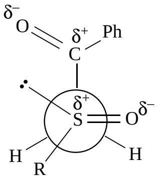
Table 4 Carbonyl frequency shifts[a] for the *cis* ($\Delta\nu_c$) and *gauche* ($\Delta\nu_g$) rotamers of the α-sulfinylacetophenones PhC(O)CH$_2$S(O)R

		n-C$_6$H$_{14}$		CCl$_4$		CHCl$_3$	
Comp.	R	$\Delta\nu_c$/cm^{-1}	$\Delta\nu_g$/cm^{-1}	$\Delta\nu_c$/cm^{-1}	$\Delta\nu_g$/cm^{-1}	$\Delta\nu_c$/cm^{-1}	$\Delta\nu_g$/cm^{-1}
1	Me	−13.0	−21.0	−11.0	−20.0	−4.5	−13.0
2	Et	−13.1	−22.1	−12.3	−21.2	−6.5	−15.2
3	Pr^i	−13.8	−22.9	−12.6	−21.9	−5.9	−14.7
4	Ph	−11.0	—	−9.0	−15.0	−2.0	−8.0
5	Bu^t	−3.6	−11.6[b] −23.4[c]	−4.4	−11.8[b] —	+1.3	−6.8[b] —

[a] $\Delta\nu_c$ and $\Delta\nu_g$ refers to the difference: $\nu_{[PhC(O)CH_2S(O)R]} - \nu_{[PhC(O)CH_3]}$, for the *cis*$_2$ and *gauche*$_3$ rotamers, respectively. [b,c] Refers to the *gauche*$_2$ and *gauche*$_3$ rotamer, respectively (see Table 2).



VIII
gauche$_3$



IX
gauche$_2$

Finally, the higher stabilization of the *cis* rotamers for α-sulfinylacetophenones **1**–**4** with respect to the *cis* rotamers of α-sulfinylacetones[1,9] (see the Introduction) may be explained by the larger relaxation of the benzene ring π-electron charge with respect to the aliphatic systems, as the $n_{O(CO)}$ ionization energy for acetophenone (9.38 eV)[33,34] and propanone (9.71 eV)[35] indicate.

The stretching frequency of the S=O band in carbon tetrachloride for compounds **1**–**4** is practically constant (1067.7–1068.8 cm^{-1}) irrespective of the inductive effect of the R substituent of the sulfinyl groups, while the $\nu_{S=O}$ for the *tert*-butyl derivative **5** is 1061.2 cm^{-1}. This result agrees with the fact that the more abundant rotamer is the higher carbonyl frequency component *cis*$_2$ for **1**–**4** and the lower carbonyl frequency component *gauche*$_2$ for **5**.

Conclusions

The preferred conformation of α-phenylsulfinylacetophenones, PhC(O)CH$_2$S(O)R (R = Me, Et, Pr^i, Ph and Bu^t) has been determined by IR spectroscopy and X-ray diffraction analyses and *ab initio* calculation. In the gas phase, in solutions of less polar solvents and in the solid state the *cis*$_2$ rotamer (*ca.* 60%) prevails for **1**–**4** over the *gauche*$_3$ rotamer (*ca.* 30%) owing to stabilizing intramolecular electrostatic and charge transfer interactions between the oppositely charged O(1) and S atoms.

In **5** the *gauche*$_2$ (*ca.* 77%) is more stable than the *cis*$_2$ rotamer (*ca.* 8%) for which a significant steric hindrance between the carbonyl oxygen atom and the bulky *tert*-butyl group takes place (structure **VI**). Thus, in order to reduce this hindrance the *tert*-butyl group moves away while the sulfur lone pair comes nearer the carbonyl oxygen lone pair. This new *cis*$_2$ conformation for **5** (structure **VII**) is destabilized by a significant electrostatic and lone pair–lone pair repulsion between the negatively charged oxygen atom and the sulfur lone pair compared with the *cis*$_2$ conformation for **1**–**4**. Furthermore, the *gauche*$_2$ rotamer of **5** (structure **IX**) which is free from steric hindrance becomes more stable than the sterically hindered *gauche*$_3$ rotamer (structure **VIII**).

In conclusion, the bulky *tert*-butyl group destabilizes the *cis*$_2$ rotamer to a higher degree than it does the *gauche*$_3$ rotamer. Thus the delicate balance of the mentioned stereoelectronic effects is responsible for the predominance of the *gauche*$_2$ rotamer in the conformational equilibrium of **5** to the detriment of the *cis*$_2$ rotamer, which in turn is the more stable rotamer for the majority of the studied acetophenone sulfoxides **1**–**4**, as expected.

Acknowledgements

The Brazilian authors thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and the Programa de Apoio Científico e Tecnológico (PADCT) for financial support to P. R. O., B. W., L. M. and for scholarships (to M. G. M., M. B. B. and M. H. Y.) and the Fundação de Amparo à Pesquisa do Estado de São Paulo for the concession of the CAD4-Mach 3 X-ray diffractometer. The Italian authors thank the Ministero della Ricerca Scientifica e Tecnologica and the Consiglio Nazionale delle Ricerche (CNR) for financial support.

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Paper 7/04219A
Received 16*th June* 1997
Accepted 15*th September* 1997