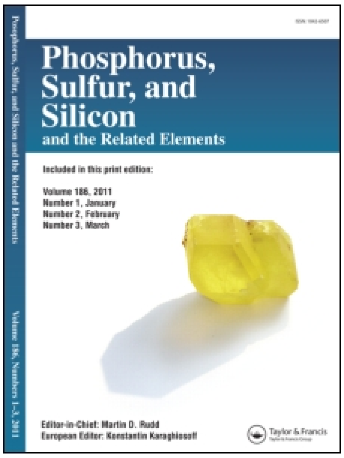

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CONFORMATIONAL AND ELECTRONIC INTERACTION STUDIES OF α-SUBSTITUTED CARBONYL COMPOUNDS. XV. α-(ARYLSULFINYL)-*p*-SUBSTITUTED ACETOPHENONES

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CONFORMATIONAL AND ELECTRONIC INTERACTION STUDIES OF α-SUBSTITUTED CARBONYL COMPOUNDS. XV. α-(ARYLSULFINYL)-*p*-SUBSTITUTED ACETOPHENONES

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The ν_{CO} IR analysis of α-(*p*-phenylsulfinyl)-*p*-substituted acetophenones X-ϕC(O)CH$_2$S(O) ϕ-Y **1–8**, being X and Y = NO$_2$, H and OMe substituents, supported by *ab initio* calculations of the α-methylsulfinyl/acetophenone (model compound) along with the X-ray geometrical data for **1, 7** and **8**, indicates the existence of the *cis*$_2$ and *gauche* rotamers for compounds **1–4** and **6**. Compounds **5, 7** and **8** present another less stable and more polar *cis*$_1$ rotamer. The *cis*$_2$ rotamer concentration for **4** (*ca.* 97% in CCl$_4$) is reduced to *ca.* 50% for **2, 3, 5–7** and to ca. 20% for **1** and **8**. This behavior is discussed in terms of $O^{\delta-}_{(CO)}$---- $S^{\delta+}_{(SO)}$ charge transfer and Coulombic interactions, which stabilize the *cis*$_1$ rotamer, and the $\pi_{CO}/\sigma^*_{C\text{-}S}$, π^*_{CO}/n_S and $\pi^*_{CO}/\sigma_{C\text{-}S}$ orbital interactions, which stabilize the *gauche* rotamers. The progressive more negative carbonyl *cis*$_2$ shifts ($\Delta\nu_c$), when X varies from NO$_2$ to H and to OMe for the same Y, along with the unexpected NAE values of the α-methylene carbon chemical shifts for compounds **1–8** give further support for the existence of a strong intramolecular complex betwen C=O and S=O dipoles which stabilizes the *cis*$_2$ rotamer. The progressive more negative carbonyl *gauche* shifts ($\Delta\nu_g$), when X varies from NO$_2$ to H and to OMe for the same Y, is in line with the higher contibution of the interaction $\pi_{CO}/\sigma^*_{C\text{-}S}$, which stabilizes the *gauche* rotamer of the title compounds.

Keywords: Conformational studies; electronic interactions; IR and ^{13}C NMR spectroscopies; α-(*p*-phenylsulfinyl)-*p*-substituted acetophenones

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INTRODUCTION

Previous reports from this laboratory on some β-ketosulfides and β-ketosulfones, $RC(O)CH_2SO_nR'$ (R = methyl, aryl; R′= Alkyl, aryl; n = 0 and 2),[1–11] by IR, ^{13}C NMR, UV, UPS spectroscopies and X-ray diffraction (for the β-ketosulfones) supported by theoretical calculations, indicated that these compounds in gas phase, in solution and in solid state (for the β-ketosulfones) prefer the *gauche* conformation.

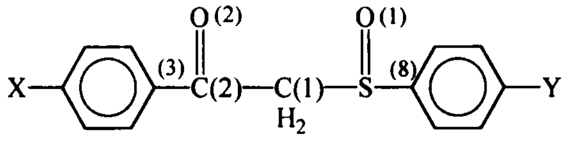
In general, the large stability of the *gauche* rotamers of the β-ketosulfones has been ascribed to the $\pi^*_{CO}/\sigma_{C\text{-}S}$ and $\pi_{CO}/\sigma^*_{C\text{-}S}$ orbital interactions. For the β-ketosulfides the $\pi^*_{CO}/\sigma_{C\text{-}S}$ orbital interaction prevails over the $\pi_{CO}/\sigma^*_{C\text{-}S}$ one, while in the case of the β-ketosulfoxides the $\pi_{CO}/\sigma^*_{C\text{-}S}$ interaction predominates over the $\pi^*_{CO}/\sigma_{C\text{-}S}$ one.

For the β-ketosulfoxides $RC(O)CH_2S(O)R'$ the *gauche* rotamer is also the more stable for the acetone derivatives (R = methyl; R′ = alkyl, aryl),[1,10] but the *cis* rotamer becomes the preferred conformation for the α-alkylsulfinylacetophenones $PhC(O)CH_2S(O)R$[12–14] (R = Me, Et, ^iPr and Ph), except for the case of R = ^tBu, for which the *gauche* conformation is the more stable one.

The peculiar stability of the *cis* rotamers of the α-sulfinylacetophenones relative to the α-sulfinylacetones has been ascribed to the increased carbonyl oxygen electronic density in the phenacyl group (due to the $\pi_{Ph} - \pi_{CO}$ conjugation), which originates intramolecular electrostatic and charge transfer interactions between the oppositively charged carbonyl oxygen and sulfinyl sulfur atoms.

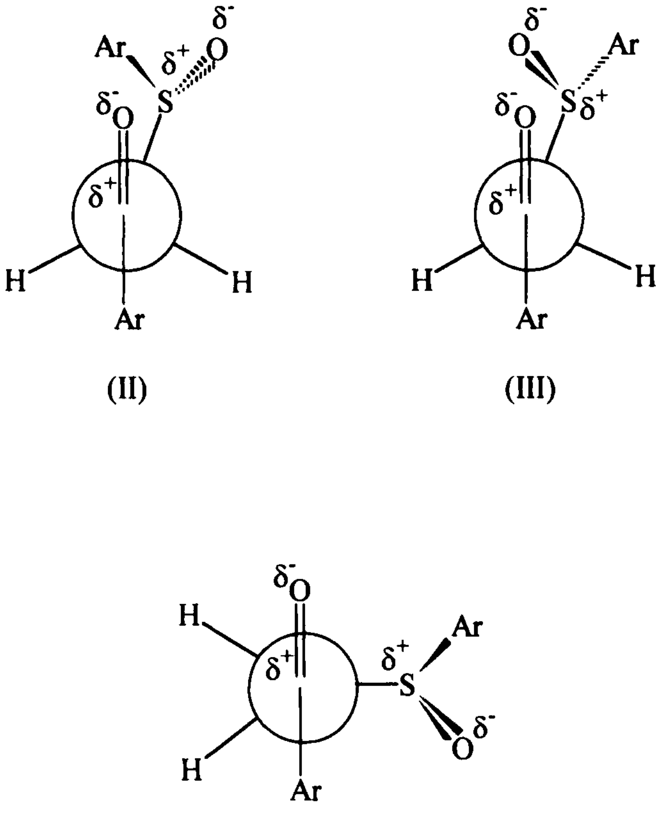
In order to further investigate the nature of the electronic and Coulombic interactions which occur in the α-sulfinylacetophenones, this paper reports the IR and ^{13}C NMR studies of some α-(*p*-phenylsulfinyl)-*p*-substituted acetophenones (Structure ***I***, Figure 1), bearing at the **para** position of the phenacyl and of the phenylsulfinyl groups electron-attracting (nitro), hydrogen and electron-donating (methoxy) substituents.

These compounds (***I***) were chosen taking into account that the orbital and Coulombic interactions, which could act in their possible *cis* (Structures II and III, Figure 2) and *gauche* (Structure ***IV***, Figure 2) rotamers, should be directly affected by changes in the conjugation envolving the *para* substituents at the phenacyl and phenylsulfinyl groups, and consequently should influence the stabilization of the referred conformers.



(I)

FIGURE 1 Structural formula of α-(*p*-phenylsulfinyl)-*p*-substituted acetophenones (being X or Y = NO_2, H and OMe substituents) with selected heavy atoms labelling



(II) (III)

(IV)

FIGURE 2 *Cis*$_2$, *cis*$_1$ and *gauche* conformations (structures II, III and IV, respectively) which should be expected for the α-arylsulfinyl-*p*-substituted acetophenones

RESULTS AND DISCUSSION

Cis-gauche Rotacional Isomerism

Table I shows the stretching frequencies and the absorbance percentage of the analytically resolved carbonyl bands for the α-(*p*-phenylsulfinyl)-*p*-substituted acetophenones **1–8** in carbon tetrachloride (fundamental and 1st overtone), chloroform and acetonitrile. The frequencies of the parent acetophenones **9–11** are included for comparison.

TABLE I Frequencies and intensities of the carbonyl stretching bands in the infrared spectra of the α-(*p*-phenylsulfinyl)-*p*-substituted acetophenones X-ϕ-C(O)-CH_2-S(O)-ϕ-Y (**1–8**) and the frequencies of the reference *p*-substituted acetophenones X-ϕ-C(O)-CH_3 (**9–11**)

Comp.	*X*	*Y*	*Conf.*[a]	CCl_4				$CHCl_3$		CH_3CN	
				ν^b	p^c	ν^d	p	ν	p	ν	p
1	NO_2	OMe	c_2	1690.7	17.4	3360.2	36.8	1693.8	28.1	1692.2	54.1
			g	1682.6	82.6	3344.8	63.2	1682.3	71.9	1681.7	45.9
2	NO_2	H	c_2	1693.4	45.7	3370.6	19.5	1692.9	42.3	1697.5	59.4
			g	1686.0	54.3	3356.4	80.5	1684.5	57.7	1687.8	40.6
3	H	OMe	c_2	1681.5	57.5	3347.0	59.3	1679.8	67.9	1682.6	66.2
			g	1673.2	42.5	3329.8	40.7	1668.9	32.1	1671.9	33.8
4[e]	H	H	c_2	1682.3	96.8	3345.8	88.4	1680.6	65.5	1685.6	48.4
			g	1676.0	3.2	3328.6	11.6	1674.7	34.5	1683.3	51.6
5	H	NO_2	c_1	1693.2	10.5	3368.2	18.3	1684.4	33.8	–	–
			c_2	1681.3	55.2	3345.5	58.5	1677.5	42.4	1683.5	66.1
			g	1673.0	34.3	3327.9	23.2	1669.8	23.7	1676.7	33.9
6	OMe	OMe	c_2	1672.8	56.4	3329.8	53.2	1669.1	52.8	1673.7	61.1
			g	1664.6	43.6	3312.7	46.8	1663.0	47.2	1663.9	38.9
7	OMe	H	c_1	1683.7	9.4	3337.2	15.8	–	–	–	–
			c_2	1673.2	42.9	3326.7	44.6	1670.4	70.0	1674.3	65.0
			g	1664.8	47.7	3312.1	39.6	1659.0	30.0	1664.8	35.0
8	OMe	NO_2	c_1	1684.5	8.3	–[f]	–	1675.4	26.9	–	–
			c_2	1672.1	24.6	3329.6	36.0	1667.3	45.7	1675.3	55.8
			g	1666.9	67.1	3313.8	64.0	1658.4	27.3	1666.9	44.2

Comp.	X	Y	Conf.[a]	CCl_4				$CHCl_3$		CH_3CN	
				ν^b	p^c	ν^d	p	ν	p	ν	p
9	NO_2			1700.5				1695.2		1669.0	
10	H			1691.2				1683.0		1686.1	
11	OMe			1683.2				1673.8		1677.3	

[a] c_1, c_2 and g, refers to the cis_1, cis_2 and *gauche* rotamers, respectively;
[b] In cm^{-1};
[c] Intensity of each component of the analytically resolved carbonyl doublet or triplet expressed in percentage of absorbance;
[d] 1st overtone;
[e] From ref. [14];
[f] See Experimental Section.

Compounds **1–4** and **6** present a doublet in all solvents. Compound **1** shows a progressive increase in the intensity of the higher frequency doublet component, in relation to the lower one, on going from carbon tetrachloride to chloroform and to acetonitrile solutions, in the same way as the solvent polarity increases. Compounds **2** and **3** show a similar but less pronounced solvent effect, whilst **6** presents a practically constant intensity ratio in all solvents.

Compound **4** displays an opposite solvent effect in relation to compounds **1–3**, *i.e.* there is a progressive increase of the intensity of the lower frequency doublet component, in relation to the higher one, as the solvent polarity increases.

Compounds **5** and **8** exhibit a triplet, whose lowest frequency component intensity decreases, in relation to the other components, on going from carbon tetrachloride to chloroform, with the disappearance of the highest triplet frequency component in acetonitrile. Compound **7** displays a triplet in carbon tetrachloride and its highest frequency triplet component vanishes in the more polar solvents (chloroform and acetonitrile), with the simultaneous increase in the intensity of the middle frequency component.

Figure 3(a-c) illustrates the solvent effect on the carbonyl band components for **1** and Figure 3(d-f) shows the opposite effect on the carbonyl band components for **4**.

The solvent effect on the intensities of the two carbonyl bands for compounds **1–3** indicates the existence of the *cis-gauche* rotational isomerism,[15a] but the observed solvent effects on the relative intensities of the carbonyl bands components, for compounds **4–8**, can not allow us to reach

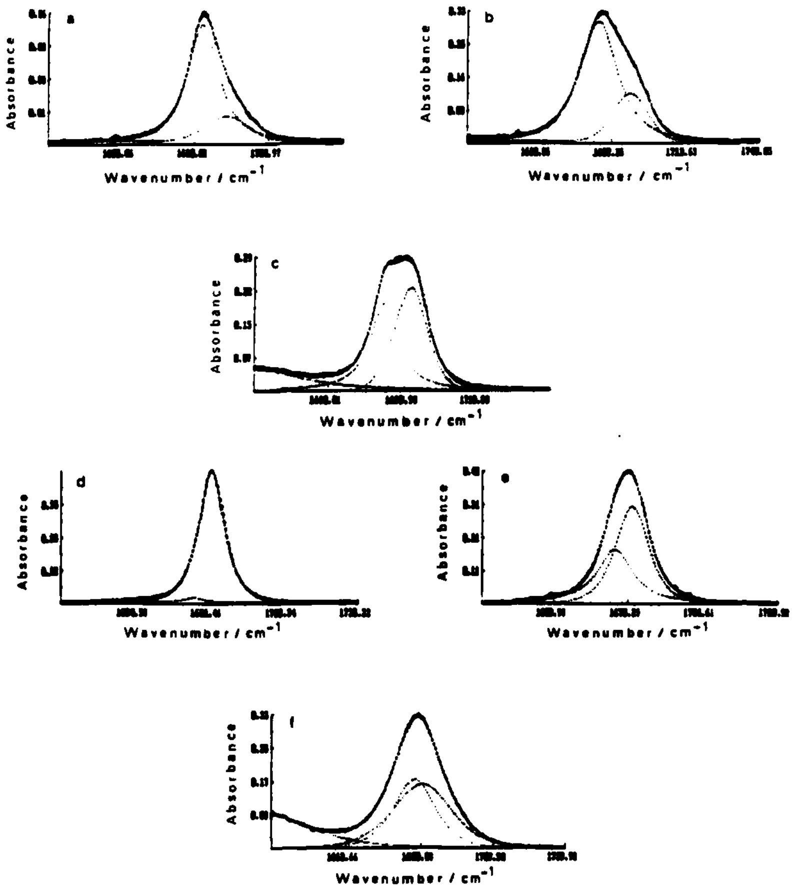


FIGURE 3 IR spectra of arylsulfinyl acetophenones **1** and **4** showing the solvent effect on the intensities of the analytically resolved carbonyl stretching bands, in carbon tetrachloride (a,d) chloroform (b,e) and acetonitrile (c,f)

a similar conclusion. However, the observation of two or three carbonyl bands in the 1st overtone region at frequencies *ca.* twice those of the fundamental, and with almost the same intensity ratios, strongly suggests that a *cis-gauche* rotational isomerism[16] shall occur for the whole series. Thus, it seems reasonable to ascribe the higher frequency component(s) of the doublet or triplet to the more polar *cis* rotamer(s) (II or II and III) and the lower one to the less polar *gauche* rotamer (IV) for compounds **1–8** (Figure 2), due to the reasons outlined below.

-ray geometrical data and the population, dipole moment and selected dihedral angles optimized for different *cis*(*c*) and *gauche* (*g*) con
ethylsulfinylacetophenone[a] ϕ-C(O)-CH$_2$-S(O)Me (**12**) at the 6–31G** level along with the X-ray data for some α-(*p*-phenylsulf
cetophenones[b] X-ϕ-C(O)-CH$_2$-S(O)-ϕ-Y (**7**,**1** and **8**)

X	*Y*		*Conf.*[c]	*P*[d]	μ[e]	*Dihedral angles*[f,g] α	β	γ	*C(2)...O(1)*[h]	*O(2*
–	–	X-ray	c_1	---	---	−8.8(7)	−178.7(5)	−71.0(4)	3.246(7)	2.87
		6–31G**	c_1	0.4	6.44	−15.7	172.4	−78.9	3.304	2.8
			c_2	63.1	5.37	8.2	−72.2	178.5	3.972	2.9
			g	26.3	2.08	88.7	−51.5	60.2	3.265	3.4
MeO	H	X-ray	c_1	–	–	−4(2)	−167(1)	86(1)	3.41(2)	2.8
NO$_2$	OMe	X-ray	c_1	–	–	−11(2)	173(1)	−75(1)	3.25(2)	2.8
OMe	NO$_2$	X-ray	*q-g*[j]	–	–	−51.1(3)	−175.1(2)	−65.7(2)	3.076(3)	2.94

4] and [17], respectively;
ribution;
on of the *cis* and *gauche* rotamers in percentage;

gles (in degrees); the labelling of the atoms are shown in Figure 1;
(2)-C(1)-S β = C(2)-C(1)-S-C(8) [C(8) corresponds to the methyl carbon for compound **12**]; γ = C(2)-C(1)-S-O(1);
van der Waals radii = 3.22Å;
van der Walls radii = 3.32Å;
the *quasi-gauche* conformation.

As the α-phenylsulfinylacetophenone **4** exhibits the same spectral characteristics of the α-alkylsulfinylacetophenones $PhC(O)CH_2S(O)R$ (R=Me, Et, and ^{i}Pr),[14] the higher frequency component of **4** can then be assigned to the *cis*$_2$ (Structure II, Figure 2) rotamer, while the lower frequency component to the *gauche* (*g*) rotamer (Structure IV, Figure 2). Moreover, the higher stability of the *cis*$_2$ rotamer of **4** in solvents of low polarity is in agreement with our *ab initio* calculations[14] for the α-methylsulfinylacetophenone (model compound **12**) (Table II). These data show that the high stability of the *cis*$_2$ rotamer is in line with a favorable geometry, which allows a short intramolecular contact between the carbonyl oxygen and the sulfur atom in relation to the sum of their van der Waals radii, due to strong attractive electrostatic and charge transfer interactions between $O_{(CO)}$ and $S_{(SO)}$ atoms. (Structure V).

Although the solvent effect on the intensities of the doublet components for **1–3** and **6** differs from that effect on **4** (Table I), the similarity of doublet frequency components for **1–3** and **6** with those of **4**, allows us to assume that the higher and lower frequency components for **1–3** and **6** should also correspond to the *cis*$_2$(c$_2$) and *gauche*(*g*) rotamers (Structures VII and VIII, Figure 4), which are also shown as Newman projections in Figure 2 (Structures II and IV, respectively).

Furthermore, the frequencies of the middle and the lowest triplet components in the spectra of compounds **5, 7** and **8**, which are close to the higher and lower frequency components of compounds **1–4** and **6**, should correspond to the *cis*$_2$(*c*$_2$) and *gauche*(*g*) rotamers too. The highest frequency triplet component, which is ca. 10 cm^{-1} higher than the middle frequency component of the triplet, in carbon tetrachloride, can be assigned to the most polar *cis*$_1$(*c*$_1$) conformer, by analogy with the model compound (Structure VI, Figure 4; see also Structure III, Figure 2). This attribution is due to the fact that both oxygen atoms, of the C=O and S=O dipoles, which are near to each other for this geometry, originate a strong repulsive Field Effect[15b] between them, which destabilizes the *cis*$_1$(*c*$_1$) conformation and increases the ν_{CO} frequency. In fact, the concentration of this rotamer in carbon tetrachloride for **5, 7** and **8** is only ca. 10%. However, similarly to α-alkylsulfinylacetophenones[14] (R = Me, Et and ^{t}Bu), the *cis*$_1$(*c*$_1$) conformation becomes the preferred conformation in the solid state of the α-arylsulfinylacetophenones[17] **1** and **7** (Table II). In the crystal, this conformation is stabilized by dipole moment coupling along with

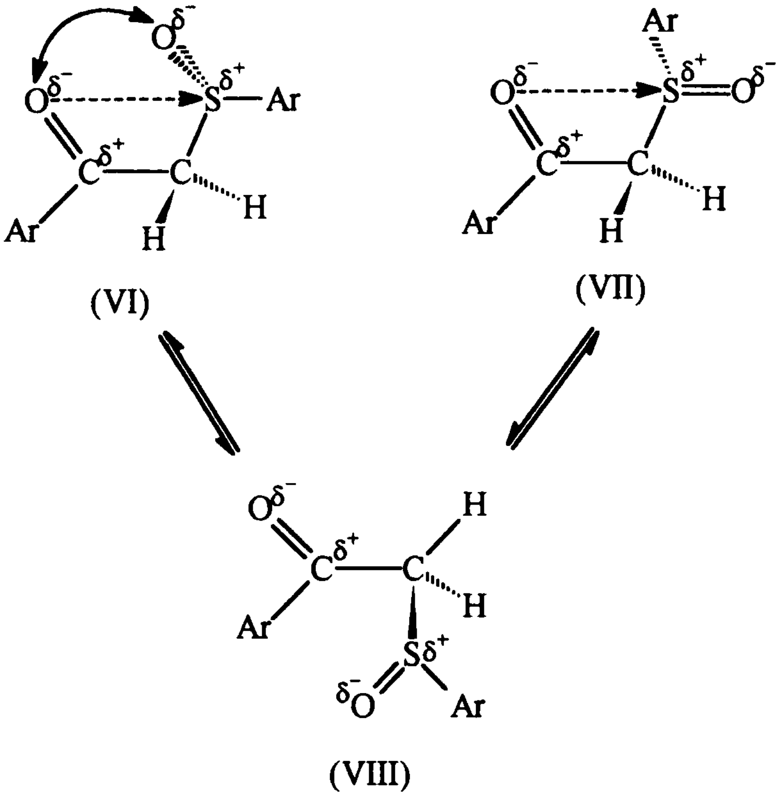


FIGURE 4 *Cis*$_1$ (VI), *cis*$_2$ (VII) and *gauche* (VIII) rotamers for the α-arylsulfininyl-*p*-substituted acetophenones

the Coulombic attraction and intramolecular charge transfer between $O_{(CO)}$ and $S_{(SO)}$ atoms, whose interatomic distances for compounds **1** and **7** are shorter than the sum of the Van der Waals radii.

The fact that the *cis*$_2$(*c*$_2$) rotamer concentration for **4** (*ca.* 97% in CCl_4) is reduced to *ca.* 50% for **2, 3, 5–7** and to *ca.* 20% for **1** and **8**, along with the appearance of a third rotamer *cis*$_1$(*c*$_1$) for **5,7** and **8** (Table I), can be rationalized as follows.

From the analysis of Figure 4, it can be concluded that for **7** (X=OMe, Y=H), **5** (X=H, Y=NO_2) and **8** (X=OMe, Y=NO_2) both the *cis*$_2$ (Structure VII) and *cis*$_1$ (Structure VI) conformers should be more stabilized (due to

$O^{\delta-}_{(CO)}$ ------ $S^{\delta+}_{(SO)}$ Coulombic and charge transfer interactions), than the same conformers for **4** (X=Y=H), either by the increase in electron density at the carbonyl oxygen atom, when X = OMe, Y = H (due to the conjugation between the methoxyl oxygen lone pair and the π system of the phenacyl group), or by the increase in positive formal charge at the sulfinyl sulfur atom, when X =H and Y= NO_2 (due to the conjugation between the sulfinyl sulfur lone pair and the π system of the *p*-nitrophenyl group). Obviously, strong $O^{\delta-}_{(CO)}$ ------ $S^{\delta+}_{(SO)}$ interaction should be expected by the simultaneous increase of electron density at the carbonyl oxygen atom and the positive charge at the sulfinyl sulfur atom when X=OMe,Y=NO_2, leading to an even larger stabilization of both *cis*$_2$ and *cis*$_1$ rotamers, with respect to the same rotamers when X=Y=H. Nevertheless, the *cis*$_1$ rotamer should be stabilized into a lesser extent than the *cis*$_2$ rotamer, in all cases analyzed, for the reasons above outlined.

It is noteworthy that the same substituents (X=OMe,Y=H); (X=H,Y= NO_2) and (X=OMe,Y= NO_2), which stabilize the *cis* rotamers of compounds **7**, **5** and **8**, respectively, also stabilize their *gauche* rotamers by the π_{CO}/σ^*_{C-S} orbital interaction with respect to the *gauche* rotamer of **4** (parent compound).

The referred π_{CO}/σ^*_{C-S} interaction can be qualitatively rationalized on the grounds of Molecular Orbital Simple Perturbation Theory[18] from the analysis of the variation of the π_{CO} and σ^*_{C-S} orbital energy levels of compounds **7**, **5** and **8**, in relation to the same orbitals of compound **4**. Figure 5 shows that the electron-donating *p*-methoxy substituent of **7** pushes up the π_{CO} energy level, which is related to the HOMO of the phenacyl group,[19,20] approximating it to the σ^*_{C-SO} level, and thus increasing the π_{CO}/σ^*_{C-S} interaction, which in its turn leads to a larger stabilization of compound **7** *gauche* rotamer in relation to the same rotamer of **4**.

For compound **5** (X=H,Y=NO_2), it is expected that the electron-attracting *p*-nitro substituent of the phenylsulfinyl group stabilizes the σ^*_{C-S} energy level bringing it closer to the π_{CO} energy level, originating a strong π_{CO}/σ^*_{C-S} interaction, and thus a larger stabilization of compound **5** *gauche* rotamer in relation to the same rotamer of **4**.

It should be pointed out that X-ray geometric data[17] for **8** (X=OMe,Y= NO_2) indicate that it assumes a *quasi-gauche* (*q-g*) conformation ($\alpha \cong 51°$), in the solid state, leading to a shortening of 0.38 Å between $O_{(CO)}$ ----$S_{(SO)}$ atoms and of 0.14 Å between the $C_{(CO)}$ ----$O_{(SO)}$ atoms with respect to the sum of their van der Waals radii (Table II). The stabilization

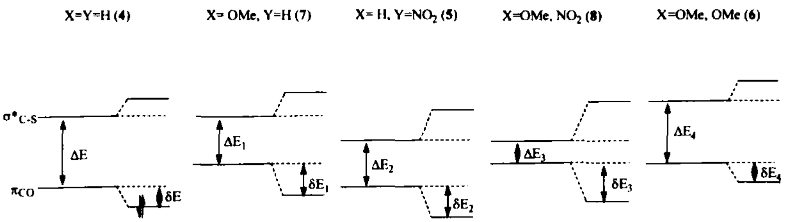


FIGURE 5 Qualitative diagram showing the π_{CO} and $\sigma^*_{C\text{-}S}$ orbital energy levels, before and after the $\pi_{CO}/\sigma^*_{C\text{-}S}$ interaction, for the *gauche* rotamer of α-arylsulfinyl acetophenones X-ϕ-C(O)CH$_2$S(O)ϕ-Y, on varying X and/or Y substituents, in comparison with the parent compound **4** (X=Y=H); being: $\delta E_3 > \delta E_2 \cong \delta E_1 > \delta E_4 \cong \delta E$

of this peculiar geometry in the solid state has been ascribed to a crossed through-space charge transfer and attractive Coulombic interaction between the oppositely charged atoms of C=O and S=O dipoles (Structure IX), which shall be also operating in solution of organic solvents. Moreover, the summing up of these interactions with the strong $\pi_{CO}/\sigma^*_{C\text{-}S}$ orbital interaction (Figure 5), which takes place into a minor extent for **5** and **7**, should stabilize the *gauche* rotamer of **8** in a greater extent than its *cis* rotamers.

From the above discussion it may be inferred for compounds **5** and **7** that the orbital interactions should stabilize the *gauche* rotamer almost to the same extent as the *cis* rotamer is stabilized by $O_{(CO)}$ ----$S_{(SO)}$ C.T. and Coulombic interactions.

Therefore, this analysis seems to be in line with the observed concentration in carbon tetrachloride of the *gauche* rotamer for **8** (ca. 70%) and for **4** and **7** (*ca.* 50%) (Table I).

In opposition to the stabilization of the *cis* rotamers for **5**, **7** and **8**, the *cis*$_2$ rotamer (Structure VII; Figure 4) should be destabilized for **2** (X=NO$_2$, Y=H), **3** (X= H, Y=OMe), and **1** (X=NO$_2$, Y=OMe), or stabilized almost to the same degree for **6** (X=OMe, Y=OMe), in comparison with the *cis*$_2$ rotamer of **4**.

In fact, there is a decrease in the electronic density at the carbonyl oxygen atom when X=NO$_2$, Y=H (due to the conjugation between the electron-attracting nitro group and the π system of the phenacyl group) and an increase in the electronic density at the sulfinyl sulfur atom when X=H, Y=OMe (due to the conjugation between the methoxyl oxygen lone pair and the π system of the phenyl group, at the phenyl sulfinyl moiety). Therefore, the $O^{\delta-}_{(CO)}$----$S^{\delta+}_{(SO)}$ Coulombic and C.T. interaction for **2** and **3** should be weaker than the same interaction for **4**. Moreover, an even weaker $O^{\delta-}_{(CO)}$----$S^{\delta+}_{(SO)}$ interaction should be expected by the simultaneous decrease of electron density at the carbonyl oxygen atom and decrease of positive formal charge at the sulfinyl sulfur atom, when X=NO_2, Y=OMe, leading to an even smaller stabilization of the *cis*$_2$ rotamer, in relation to the same rotamer when X=Y=H.

In compound **6**, the *p*-methoxy substituent at the phenacyl group increases the electron density of the carbonyl oxygen atom favoring the $O_{(CO)}$----$S_{(SO)}$ interaction, but the same substituent at the phenylsulfinyl group leads to a decrease in the positive formal charge at the sulfinyl sulfur atom, making difficult the referred interaction. Therefore, the *cis* conformer of **6** seems to be stabilized almost to the same extent than the *cis* rotamer of **4** (parent compound).

From the above analysis, it seems clear that for compounds **1–4** and **6** only the *cis*$_2$ rotamer should be present in solution, once the *cis*$_1$ rotamer would have an even lower stability.

On the other hand, the same substituents (X= NO_2, Y=H), (X= H, Y=OMe) and (X=OMe, Y=NO_2) which destabilize the *cis* rotamers of compounds **2, 3** and **1** respectively, stabilize their *gauche* rotamers by $\pi^*_{CO}/\sigma_{C\text{-}SO}$ and π^*_{CO}/n_S orbital interactions with respect to the *gauche* rotamer of **4**.

Figure 6 shows that the electron-attracting *p*-nitro substituent of **2** stabilizes the π^*_{CO} energy level, which is related to the LUMO of the phenacyl group,[19,20] acts approximating it to the $\sigma_{C\text{-}S}$ (Figure 6a) and to the sulfur lone pairs n_S (Figure 6b) energy levels, making easier both the π^*_{CO}/n_S and $\pi^*_{CO}/\sigma_{C\text{-}S}$ orbital interactions leading to a larger stabilization of the *gauche* rotamer of **2** in relation to the same rotamer of **4**.

For **3**, the electron-donating *p*-methoxy substituent at the phenylsulfinyl group destabilizes both the $\sigma_{C\text{-}S}$ and n_S orbitals, bringing them closer to the π^*_{CO} energy level making easier both the $\pi^*_{CO}/\sigma_{C\text{-}S}$ and π^*_{CO}/n_S orbital interactions, leading to a larger stabilization of the *gauche* rotamer of **3** in relation to that of **4**.

In the case of **1**, for which the energy levels of both pair of orbitals (π^*_{CO} and $\sigma_{C\text{-}S}$, π^*_{CO} and n_S), are closer to each other with respect to the same orbitals of **4**, even stronger π^*_{CO}/n_S and $\pi^*_{CO}/\sigma_{C\text{-}S}$ interactions should occur, leading to a more stable gauche conformer for **1** (*ca.* 80%),

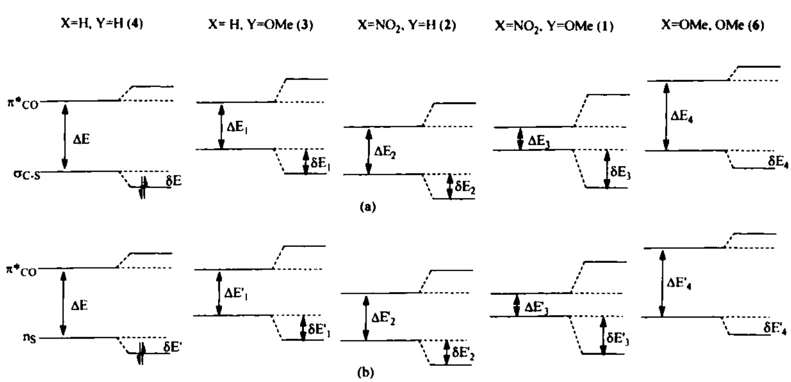


FIGURE 6 Qualitative diagram showing the π^*_{CO}, $\sigma_{C\text{-}S}$ and n_S orbital energy levels, before and after $\pi^*co/\sigma_{C\text{-}S}$ (a) and π^*co/n_S (b) interactions, for the *gauche* rotamer of α-arylsulfinyl acetophenones X-ϕ-C(O)CH$_2$S(O)-ϕ-Y, on varying X and/or Y substituents, in comparison with the parent compound **4** (X=Y=H); being: $\delta E_3 > \delta E_2 \cong \delta E_1 > \delta E_4 \cong \delta E$ [for (a)], and $\delta E'_3 > \delta E'_2 \cong \delta E'_1 > \delta E'_4 \cong \delta E'$ [for (b)]

in comparison with the same conformer of **2** and **3**. Therefore, the destabilization of the *cis*$_2$ rotamer of **2** and **3**, with the simultaneous stabilization of their *gauche* rotamers with respect to **4**, is in line with the fact that their concentration increases to *ca.* 50% for **2** and **3**. Moreover, the predominance of the *gauche* rotamer for **1** (*ca.* 80%) is in agreement with the more pronounced destabilization of the *cis* rotamer and the larger stabilization of the *gauche* rotamer of this compound, in comparison with **2** and **3**.

From Figures 5 and 6, it can be seen that the *gauche* rotamer of 6 which bears the electron-donor *para*-methoxy substituents both at the phenacyl and at the phenylsulfinyl moieties, neither the $\pi_{CO}/\sigma^*_{C\text{-}S}$ nor the π^*_{CO}/n_S and $\pi^*_{CO}/\sigma_{C\text{-}S}$ orbital interactions are favored with respect to the same interactions in the gauche rotamer of **4** (parent compound). Furthermore this behavior is similar to that observed for the *cis* rotamer of **6**, which is not stabilized with respect to the same rotamer of **4**. However, from the experimental data which indicate that the *gauche* rotamer concentration for **6** is *ca.* 50%, it may be inferred that the summing up of the *gauche* orbital interactions should contribute almost to the same extent as the $O^{\delta-}_{(CO)}$----$S^{\delta+}_{(SO)}$ interaction, which takes place in the *cis* rotamer.

CARBONYL STRETCHING FREQUENCY SHIFTS

Table III shows the carbonyl frequency shifts ($\Delta\nu$) in carbon tetrachloride, for the *cis* (c_1 and c_2) and *gauche* (g) rotamers of the β-ketosulfoxides **1–8** in relation to the parent compounds **9–11**. It can be noticed that both *cis*$_2$ and *gauche* shifts are negative, being the *gauche* shifts twice as larger than the *cis*$_2$ ones. The *cis*$_1$ shifts for compounds **5, 7** and **8** are slightly positive.

TABLE III Carbonyl frequency shifts[a] for the *cis* ($\Delta\nu_c$) and *gauche* ($\Delta\nu_g$) rotamers of the α–(arylsulfinyl)-*p*-substituted acetophenones X-ϕ-C(O)-CH_2-S(O)-ϕ-Y, in CCl_4

Compound	*X*	*Y*	*CCl_4*	
			$\Delta\nu_c^b$	$\Delta\nu_g$
1	NO_2	OMe	−9.8 (c_2)	−17.9
3	H	OMe	−9.8 (c_2)	−18.0
6	OMe	OMe	−10.4 (c_2)	−18.6
2	NO_2	H	−7.1 (c_2)	−14.5
4	H	H	−8.9 (c_2)	−15.0
7	OMe	H	+0.5 (c_1)	−18.4
			−10.0 (c_2)	
5	H	NO_2	+2.0 (c_1)	−18.3
			−9.9 (c_2)	
8	OMe	NO_2	+1.3 (c_1)	−16.3
			−11.1 (c_2)	

[a] $\Delta\nu_c$ and $\Delta\nu_g$ refer to the difference: ν[X-ϕ-C(O)-CH_2-S(O)-ϕ-Y] – ν[X-ϕ-C(O)-CH_3], varying X for the same Y, in cm^{-1};
[b] c_2 and c_1 refer to the *cis*$_2$ and *cis*$_1$ rotamers, respectively.

The abnormal *cis* shifts for the *cis*$_2$ rotamer in the title compounds along with their progressively more negative values when X changes from electron-attracting (NO_2) to hydrogen and to electron-donating (OMe) substituents, for the same Y, give support to the existence of an intramolecular complex between C=O and S=O dipoles, which stabilizes the *cis*$_2$ rotamer (Structure VII, Figure 4) as discussed in the previous Section, leading to a decrease of the carbonyl force constants, and thus in the frequencies in the same direction.

The slightly positive *cis* shifts for the *cis*$_1$ rotamer in compounds **5, 7** and **8** support the fact that its geometry is similar to that of the α-methylsulfinylacetophenone obtained by *ab initio* calculations and X-ray diffraction (Structure VI, Figure 4 and Table II).

As pointed out, in the previous Section, the oxygen atoms of the C=O and S=O dipoles closeness to each other (Structure VI) should originate a strong repulsive Field Effect[15b] between them, and a significant rising in the carbonyl frequency, leading to the *cis*$_1$ shifts. Nevertheless, the observed small positive *cis*$_1$ shifts is an additional evidence that the Repulsive Field Effect is attenuated by the occurrence of the $O^{\delta-}_{(CO)}$----$S^{\delta+}_{(SO)}$ attractive electrostatic and charge transfer interactions, which are responsible for the stabilization of the *cis*$_1$ conformer in solution of organic solvents. Moreover the fact that $O_{(CO)}$----$S_{(SO)}$ distances of the *cis*$_1$ rotamer in the crystal and gas phase of the model compound **12** (2.87 Å) and in the crystal of **7** (2.88 Å), which are shorter than the sum of the Van der Waals radii, corroborates this proposition (Table II).

The significant negative *gauche* shifts for the β-ketosulfoxides **1–8** are in agreement with the simultaneous occurrence ($\pi^*_{CO}/\sigma_{C\text{-}S}$; π^*_{CO}/n_S) and ($\pi_{CO}/\sigma^*_{C\text{-}S}$) orbital interactions (being the latter interaction the more important one).[2] These interactions prevail, in a larger extent, over the -I effect of the arylsulfinyl groups ($\sigma_{I\ (S(O)Ph)} = 0.52$)[21] leading to a decrease of the carbonyl force constant and hence in the ν_{CO} frequencies of the *gauche* rotamers of **1–8**, in relation to the parent acetophenones **9–11**.

The progressively more negative carbonyl *gauche* shifts, when X changes from NO_2 to H and to OMe substituents, for the same Y, is in line with the higher contribution of the $\pi_{CO}/\sigma^*_{C\text{-}SO}$ interaction in the β-ketosulfoxides.[2]

In fact there is a progressive destabilization of the π_{CO} orbital energy level, which is related to the HOMO of the phenacyl group[19,20] on going from electron-attracting (NO_2) to electron-donating (OMe) substituents approximating it to the $\sigma^*_{C\text{-}SO}$ orbital (Figure 7). This originates a progressively stronger $\pi_{CO}/\sigma^*_{C\text{-}SO}$ orbital interaction, and thus a progressive lowering in the π_{CO} bond order, and thus in the carbonyl frequencies.

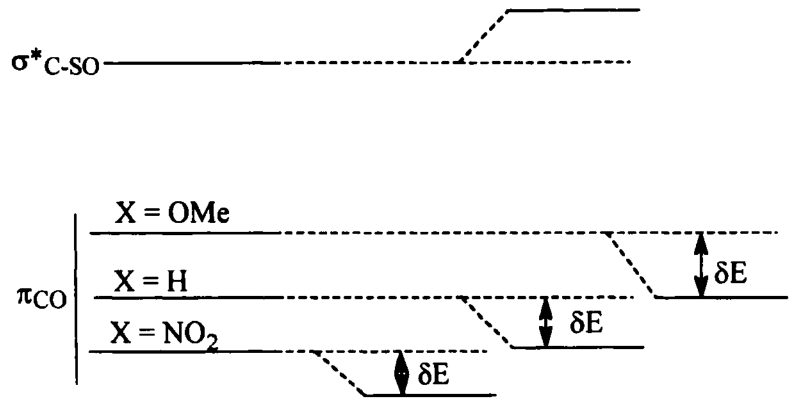


FIGURE 7 Qualitative energy level diagram showing the $\pi_{CO}/\sigma^*_{C\text{-}S}$ orbital interaction for the *gauche* rotamers of the α-(arylsulfinyl)-*p*-substituted acetophenones varying X for the same Y substituent

^{13}C NMR SPECTROSCOPY

Table IV shows the ^{13}C NMR data for the methylene and carbonyl carbons (in -C(O)CH$_2$- group) of the α-(*p*-phenylsulfinyl)-*p*-substituted acetophenones **1–8**. This Table also presents the calculated α-methylene carbon chemical shifts for the title compounds along with the Non Additivity Effect[22] (NAE), i.e. the difference between the experimental and the calculated α-methylene chemical shifts.

It is well known that the variation on conjugation in the carbonyl groups in the *p*-substituted aromatic ketones[23] does not affect significantly the shielding on the carbonyl carbon. In fact, a practically constant carbonyl chemical shift of *ca.* 190 ppm for the β-ketosulfoxides **1–8** can be observed in Table IV. It should be pointed out that the corresponding β-ketosulfides[6] X-ϕ-C(O)CH$_2$S-ϕ-Y also show an almost constant carbonyl carbon chemical shift of *ca.* 193 ppm. Therefore, the nearly constant upfield shift of *ca.* 3.0 ppm for the carbonyl carbon, on going from β-ketosulfides to β-ketosulfoxides, may be ascribed, at least in part, to the higher inductive effect of the arylsulfinyl substituent ($\sigma_{I\ (S(O)Ph)} = 0.52$)[21] in relation to the arylthio substituent ($\sigma_{I\ (SPh)} = 0.25$).[21]

TABLE IV ^{13}C NMR Chemical Shifts[a] for the carbonyl and α–methylene carbons (in -C(O)-CH_2-), and NAE valucs ($\Delta\delta_{CH2}$), of α-(arylsulfinyl)-*p*-substituted acetophenoncs X-ϕ-C(O)-CH_2-S(O)ϕ-Y, in $CDCl_3$

X	*Y*	*Comp.*	δ_{CO}	δ_{CH2}	$\Delta\delta_{CH2}$[b]
NO_2	OMe	**1**	190.15	65.44	−7.28
				72.72[c]	
NO_2	H	**2**	190.02	65.15	−7.33
				78.88	
H	OMe	**3**	191.32	65.93	−6.42
				72.35	
H	H	**4**	191.17	65.84	−6.67
				72.51	
H	NO_2	**5**	190.78	65.46	−6.86
				72.32	
OMe	OMe	**6**	189.47	65.69	−6.36
				72.05	
OMe	H	**7**	189.40	65.70	−6.51
				72.21	
OMe	NO_2	**8**	188.91	65.31	−6.71
				72.02	

[a] In ppm relative to TMS.

[b] $\Delta\delta = \delta_{exp} - \delta_{calc}$.

[c] The second entries are those calculated using substituent chemical shifts.

The computed α–methylene carbon chemical shifts[24] for the α-(*p*-phenylsulfinyl)-*p*-substituted acetophenones were obtained through equation (1), where α_{Z_1} and α_{Z_2} are the α effects of the Z_1 and Z_2 substituents and −2.3 is the chemical shift for the methane carbon atom.

$$\delta_{CH_2} = -2.3 + \alpha_{Z_1} + \alpha_{Z_2} \qquad (1)$$

The effects of α_Z of Z_1 and Z_2 substituents were estimated from equation 2 *i.e.* from the chemical shifts of the methyl carbon for the H_3C-Z molecules presented in Table V and the chemical shift of methane carbon.

$$\alpha_Z = \delta_{CH_3}(H_3C\text{-}Z) - \delta_{CH_4} \qquad (2)$$

TABLE V ^{13}C NMR chemical shifts for the methyl carbons[a] of H_3C-Z, in $CDCl_3$, and the α effect of the Z group (α_Z)

H_3C-*Z*	*Z*	δ_{CH3}	α_Z
H_3C-C(O)-ϕ-NO_2	-C(O)-ϕ-NO_2	26.78	29.08
H_3C-C(O)-ϕ	-C(O)-ϕ	26.41	28.71
H_3C-C(O)-ϕ-OMe	-C(O)-ϕ-OMe	26.11	28.41
H_3C-S(O)-ϕ-NO_2	-S(O)-ϕ-NO_2	43.61	45.91
H_3C-S(O)-ϕ[b]	-S(O)-ϕ	43.8	46.1
H_3C-S(O)-ϕ-OMe	-S(O)-ϕ-OMe	43.64	45.94

[a] In ppm relative to TMS.
[b] From ref. 25.

For instance, the calculated δ_{CH2} for α-(*p*-nitrophenylsulfinyl)-*p*-methoxyacetophenone **8** is:

$$\delta_{CH_2} = -2.3 + 28.41 + 45.91 = 72.02; \delta_{CH_2(exp.)} = 65.31 \text{ ppm}$$

Table IV also shows that the mean Non Additivity Effect Values (Δδ) for the α-methylene carbon chemical shifts for the β-ketosulfoxides (Δδ = −6.8 ppm) is close, but slightly smaller than the corresponding mean value for the β-ketosulfides[6] (Δδ = −7.4 ppm). These NAE values are still lower than those for the ω-iodoacetophenones[26] whose (Δδ) mean value is −15.0 ppm. This behavior is similar to that previously observed for the α-arylthioacetophenones,[6] and also suggests a decreasing contribution of the $\pi^*_{CO}/\sigma_{C\text{-}SO}$ interaction for the *gauche* rotamers of the α-arylsulfinylacetophenones **1–8**, due to the simultaneous occurrence of the $\pi_{CO}/\sigma^*_{C\text{-}SO}$ orbital interaction, which leads to a decrease in the NAE values.

Moreover, our previous work[2] showed that while in the β-ketosulfides the $\pi^*_{CO}/\sigma_{C\text{-}S}$ prevails over the $\pi_{CO}/\sigma^*_{C\text{-}S}$ interaction, in the case of the β-ketosulfoxides the $\pi_{CO}/\sigma^*_{C\text{-}S}$ prevails over the $\pi^*_{CO}/\sigma_{C\text{-}S}$ interaction, for their *gauche* rotamers.

Therefore, it should be expected in the β-ketosulfoxide series **1–8** a significantly smaller NAE mean value in relation to that of the β-ketosulfides. However, the slightly smaller NAE mean value (*ca.* 0.6 ppm) for the β-ketosulfoxides, in relation to the β-ketosulfides, support the fact that the β-ketosulfides in chloroform solution exist mostly in the *gauche* conformation, while the β-ketosulfoxides present in this solvent a *gauche* concentration close to 50% (Table I). Although, the *cis* conformation of the β-ketosulfoxides precludes the occurrence of the $\pi_{CO}/\sigma^*_{C\text{-}S}$ interaction, it is propitious for the $O_{(CO)}$ ----$S_{(SO)}$ interaction, which increases the electronic density at the sulfinyl sulfur atom leading to some additional shielding on the α-methylene carbon atom.

Consequently, the closeness between the NAE mean values of the α-methylene carbon for the β-ketosulfoxides and for the β-ketosulfides gives further support for the existence of the $O^{\delta-}{}_{(CO)}$----$S^{\delta+}{}_{(SO)}$ Coulombic and charge transfer interaction in the *cis* rotamer of the β-ketosulfoxides **1–8**.

EXPERIMENTAL

Materials

All solvents for spectrometric measurements were spectrograde and were used without further purification. α-(*p*-Phenylsulfinyl)-*p*-substituted acetophenones X-ϕC(O)CH_2S(O)ϕ-Y **1–8** were prepared through the following procedure. To a solution of α-(*p*-phenylthio)-*p*-substituted acetophenone[6] cooled at 0° C an equivalent amount of 30% hydrogen peroxide was added dropwise. The stirred reaction mixture was kept at room temperature until all the ketosulfide has been reacted. After the reaction work up, the pure solids were obtained from recrystallization in methanol. The physical, ^{1}H NMR and elemental analysis data of the obtained compounds are presented in Table VI. The arylsulfinylacetophenones **1, 2, 5, 6** and **8** are new compounds. Although compound 3 has already been described in the literature, its melting point deviates significantly from ours. The arylsulfynilmethanes $H_3CS(O)\phi\text{-}Z$ (Z=NO_2, H and OMe) were obtained by literature procedures.[27]

TABLE VI Physical, ^1H NMR and elemental analysis data for the α-(*p*-phenylsulfinyl)-*p*-substituted acetophenoncs X-ϕ-C(O)-CH_2-S(O)-ϕ-Y

Comp.	*X*	*Y*	*M.P.(°C)*	*^1H NMR*[a]	*Molecular formula*		*Analysis*		
							C	*H*	*N*
1	NO_2	OMe	106–116	8.25(d, 2H, Ar_1[b], J=8.9Hz), 8.01(d, 2H, Ar_1, J=8.9Hz), 7.55(d, 2H, Ar_2[c], J=8.9Hz), 6.96(d, 2H, Ar_2, J=8.9Hz), 4.50(d, 1H, CH_2, J=13.6Hz), 4.14(d, 1H, CH_2, J=13, 6Hz), 3.80(s, 3H, OCH_3)	$C_{15}H_{13}NO_5S$	Calc	56.42	4.10	4.39
						Found	56.77	3.95	4.73
2	NO_2	H	124–126	8.35(d, 2H, Ar_1, J=8.9Hz), 8.14(d, 2H, Ar_1, J=8.9Hz), 7.41–7.26 (m, 5H, Ar_2), 6.33(s, 1H, vinyl CH)[d], (4.10bs, 2H, CH_2)[e]	$C_{14}H_{11}NO_4S$	Calc	58.18	3.83	4.84
						Found	58.15	3.81	4.41
3	H	OMe	66–68 95–96[f]	7.86(d, 2H, Ar_1, J=7.3Hz), 7.60(d, 2H, Ar_2, J=8.9Hz), 7.57(t, 1H, Ar_1, J=7.3Hz), 7.43(t, 2H, Ar_1, J=7.3Hz), 6.97(d, 2H, Ar_2, J=8.9Hz), 4.58 (d, 1H, CH_2, J=14Hz), 4.28(d, 1H, CH_2, J=14Hz), 3.83(s, 3H, OCH_3)	$C_{15}H_{14}O_3S$	Calc	65.67	5.14	
						Found	65.85	5.00	
4	H	H	75–78 76–77[g] 70–71[f]	7.90–7.41(m, 10H, Ar_1 and Ar_2) 4.57(d, 1H, CH_2, J=14.2Hz), 4.30(d, 1H, CH_2, J=14.2Hz)	$C_{14}H_{11}O_2S$	calc.	68.83	4.95	
						Found	68.87	4.79	
5	H	NO_2	126–132	8.36(d, 2H, Ar_2, J=8.9Hz), 7.91(d, 2H, Ar_2, J=8.9Hz), 7.88(d, 2H, Ar_1, J=7.3Hz), 7.63(t, 1H, Ar_1, J=7.3Hz), 7.48(t, 2H, Ar_1, J=7.3Hz), 4.61 (d, 1H, CH_2, J=14.6Hz), 4.44(d, 1H, CH_2, J=14.6Hz)	$C_{14}H_{11}NO_4S$	Calc.	58.12	3.83	4.84
						Found	58.22	3.80	4.90
6	OMe	OMe	63–67	7.86(d, 2H, Ar_1, J=8.9Hz), 7.62(d, 2H, Ar_2, J=8.8Hz), 6.98(d, 2H, Ar_2, J=8.8Hz), 6.91(d, 2H, Ar_1, J=8.9Hz), 4.53(d, 1H, CH_2, J=13.9Hz), 4.22(d, 1H, CH_2, J=13.9Hz), 3.86(s, 3H, OCH_3), 3.82(s, 3H, OCH_3)	$C_{16}H_{16}O_4S$	Calc	63.14	5.30	
						Found	63.17	5.40	

	Y	M.P.(°C)	^{1}H NMR^{a}	Molecular formula		Analys	
						C	H
Me	H	84–88 79–80^{f}	7.86(d, 2H, Ar_1, J=9.0Hz), 7.71–7.65(m, 2H, Ar_2), 7.52–7.47(m, 3H, Ar_2), 6.90(d, 2H, Ar_1, J=9.0H_z), 4.24(d, 1H, CH_2, J=14.0Hz), 3.92 (d, 1H, CH_2, J=14.0Hz), 3, 85(s, 3H, OCH_3)	$C_{15}H_{14}O_3S$	Calc. Found	65.76 65.61	5.1 5.0
Me	NO_2	170–175	8.35(d, 2H, Ar_2, J=8.8Hz), 7.90(d, 2H, Ar_1, J=8.8Hz), 7.85 (d, 2H, Ar_2, J=8.8Hz), 6.93(d, 2H, Ar_1, J=8.8Hz), 4.56(d, 1H, CH_2, J=14.5Hz), 4.38(d, 1H, CH_2, J=14.5Hz), 3.88(s, 3H, OCH_3)	$C_{15}H_{13}NO_6S$	Calc. Found	56.42 55.95	4.1 4.0

ical shirts in ppm relative to TMS and coupling constants in Hz, for $CDCl_3$ solutions.

Ar_2 refer to the phenacyl and phenylsulfinyl groups, respectively.

enolic and keto forms, respectively (see Experimental Section).

fs. [28] and [29], respectively.

IR Measurements

The IR spectra were obtained in a FT-IR Nicolet Magna 550 Spectrometer, with 1.0 cm^{-1} resolution. For acetophenones **1–11** the carbonyl stretching region (1800–1600 cm^{-1}) was recorded in 2.0×10^{-2} $mol.dm^{-3}$ carbon tetrachloride, chloroform and acetonitrile solutions, using 0.519 mm sodium chloride cell. For the carbonyl 1st overtone region (3600–3100 cm^{-1}) spectra were obtained in 2.0×10^{-2} $mol.dm^{-3}$ carbon tetrachloride solutions, using 1.00 cm quartz cell. The overlapped carbonyl bands were computationaly deconvoluted as previously described.[11] Due to the low solubility of **8** in carbon tetrachloride (conc. $\cong 10^{-3} mol.dm^{-3}$) it was not possible to resolve the highest frequency carbonyl triplet component in the 1st overtone region. The relative concentrations of the *cis-gauche* rotamers were estimated from the absorbance percentage taken at the absorption maxima of the two or three components of the carbonyl band, assuming that the molar absorptivity coefficients of the two or three rotamers are the same.

NMR measurements

The conditions for recording ^{1}H and ^{13}C NMR spectra have been described elsewere.[11] Compound **2** exists in chloroform solution largerly in the intramolecular associated enol form [$IR_{(CHCl3)}$: $\nu_{(OH)} = 3472$ cm^{-1} (strong band)]. Thus, the double doublet of the α-methylene carbon which appears normally in the range 4.10–4.60 ppm, becomes a broad singlet at 4.10 ppm due to fast proton exchange with the enolic form.

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