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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

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CONFORMATIONAL AND ELECTRONIC INTERACTION STUDIES OF α -SUBSTITUTED CARBONYL COMPOUNDS. XIV. α -(ARYLSULFONYL)-*p*-SUBSTITUTED ACETOPHENONES^[1]

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To cite this Article Olivato, Paulo R. , Guerrero, Sandra A. and Rittner, Roberto(1997) 'CONFORMATIONAL AND ELECTRONIC INTERACTION STUDIES OF α -SUBSTITUTED CARBONYL COMPOUNDS. XIV. α -(ARYLSULFONYL)-*p*-SUBSTITUTED ACETOPHENONES^[1]', Phosphorus, Sulfur, and Silicon and the Related Elements, 130: 1, 155 — 174

To link to this Article: DOI: 10.1080/10426509708033706

URL: <http://dx.doi.org/10.1080/10426509708033706>

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CONFORMATIONAL AND ELECTRONIC INTERACTION STUDIES OF α -SUBSTITUTED CARBONYL COMPOUNDS. XIV. α -(ARYLSULFONYL)-*p*-SUBSTITUTED ACETOPHENONES^[1]

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(Received 7 May 1997; Revised 27 August 1997; In final form 27 August 1997)

The ν_{CO} IR analysis of α -(*p*-phenylsulfonyl)-*p*-substituted acetophenones $\text{X}-\phi\text{C}(\text{O})\text{CH}_2\text{S}(\text{O})_2\phi-\text{Y}$ **1–8**, being X and Y = NO₂, H and OMe substituents, supported by Molecular Mechanics data of the α -methylsulfonylacetophenone (model compound), indicates the existence of the *cis/gauche* rotational isomerism. The less polar *gauche*₂ rotamer is the more stable (conc. $\cong$ 90%) and the more polar *cis* rotamer is the less stable one along the series. Compounds **4** (X = Y = H) and **3** (X = H, Y = OMe) present another less stable and rather polar *gauche*₁ rotamer. The almost constant carbonyl *gauche*₂ shifts ($\Delta\nu_{\text{k}2}$) together with the quasi-invariability of the *cis/gauche* ratios, when X varies and Y is fixed, indicates a very nearly constant summing up of $\pi^*_{\text{CO}}/\sigma_{\text{C-SO}_2}$ and $\pi_{\text{CO}}/\sigma^*_{\text{C-SO}_2}$ orbital interactions. The progressive stabilization of the *gauche*₂ rotamer when X is fixed and Y changes from NO₂ to OMe substituents, along with the parallel decrease of the positive sulfonyl asymmetric frequency shifts ($\Delta\nu_{\text{SO}_2(\text{as})}$) is discussed in terms of the progressive contribution of the $\text{O}(\text{SO}_2) \rightarrow \text{C}(\text{CO})$ electrostatic and charge transfer interactions. Additional support for the proposed interactions is given by the large NAE mean value for the α -methylene carbon chemical shifts together with the upfield shift of the β -ketosulfones mean carbonyl carbon chemical shifts in relation to that of the β -ketosulfoxides.

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

INTRODUCTION

Previous reports from this laboratory on some β -ketosulfides, β -ketosulfoxides and β -ketosulfones $\text{RC}(\text{O})\text{CH}_2\text{SO}_n\text{R}'$ (R = methyl, aryl; R' = alkyl, aryl; n

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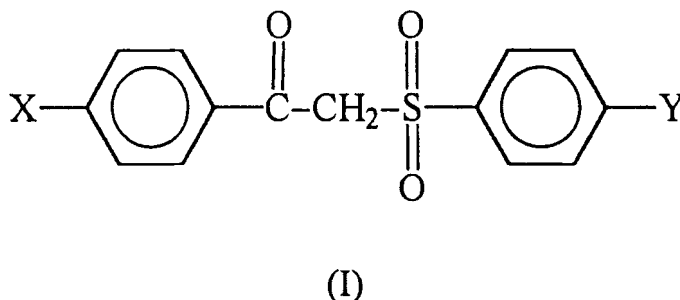


FIGURE 1 Structural formula of the α -(*p*-phenylsulfonyl)-*p*-substituted acetophenones, being X or Y = NO₂, H and OMe substituents.

= 0 and 2)^[2-10] and (R = methyl; R' = alkyl, aryl; n = 1)^[2,11] by IR, ¹³C NMR, U.V., UPS spectroscopies and X-ray diffraction (for the β -ketosulfones) supported by Molecular Mechanics, semi-empirical and *ab-initio* calculations, indicated that these compounds in gas phase, in solution and in solid state (for the β -ketosulfones) prefer the *gauche* conformation relative to the *cis* one.

In general, the large stability of the *gauche* rotamers of the β -ketosulfones has been ascribed to the π^*_{CO}/σ_{C-S} and π_{CO}/σ^*_{C-S} orbital interactions. For the β -ketosulfides the π^*_{CO}/σ_{C-S} orbital interaction prevails over the π_{CO}/σ^*_{C-S} one, while in the case of the β -ketosulfoxides the π_{CO}/σ^*_{C-S} interaction predominates over the π^*_{CO}/σ_{C-S} one.

Our theoretical, UPS and X-ray studies of some β -ketosulfones,^[8,10] which include the α -arylsulfonyl-*p*-substituted acetophenones **1**, **4** and **7** (see below), in gas phase and solid state, indicated that besides both π^*_{CO}/σ_{C-S} and π_{CO}/σ^*_{C-S} interactions there is an additional stabilization of the *gauche* rotamers, due to crossed electrostatic and charge transfer interactions between oppositely charged atoms i.e. O_(SO₂) → C_(CO) and O_(CO) → S_(SO₂).

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

These model compounds were chosen taking into account that the orbital and Coulombic interactions, which could act in the *cis* and *gauche* rotamers of the title compounds, should be directly affected by the variations on the conjugation involving the *para* substituents at the phenacyl and phenylsulfonyl groups, and consequently should influence the stabilization of the referred rotamers.

RESULTS AND DISCUSSION

Cis-gauche Rotational Isomerism

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

Compounds **1, 2, 5–8** show doublets in all solvents. Compound **4** exhibit triplets in all solvents, while compound **3** displays a triplet only in carbon tetrachloride, losing its central component in the polar solvents chloroform and acetonitrile. Figure 2 illustrates the solvent effect on the triplet components of **4**.

The absorbance ratio between the higher and lower frequency components for **1, 2, 5–8**, and between the higher and the sum of the two lower frequency components for **4** increases progressively from carbon tetrachloride to chloroform, and from these to acetonitrile solutions, in the same way as the solvent polarity increases. It has to be noted that just doublets are observed in chloroform and acetonitrile solutions for compound **3**, and then these absorbance ratios involve only their higher and lower frequency components. These solvent effects and the occurrence of two or three carbonyl bands in the 1st overtone region at frequencies *ca.* twice those in the fundamental and with almost the same intensity ratios strongly indicate that compounds **1–8** display a *cis*(II)-*gauche*(III) (Figure 3) rotational isomerism.^[12a,13] The rotamer attribution of each carbonyl band component for compounds **1–8** (Table I) has been done as outlined below.

Our 3–21 G* *ab-initio* calculations^[10] for the α -arylsulfonyl-*p*-substituted acetophenones **4, 7** and **1** have indicated that these compounds exist in the gas phase predominantly in the *gauche* conformation, and from X-ray analyses^[10] that this conformer is the only one present in the solid state. Moreover, compounds **4, 7** and **1** *gauche* geometries are very similar to that previously obtained by Molecular Mechanics Calculation (MMC) for the α -methylsulfonylacetophenone.^[4] In fact Table II shows that the MMC dihedral angles θ and ϕ of the most stable *gauche* rotamer g_2 of the α -methylsulfonylacetophenone compare very well with the corresponding *ab-initio* 3–21G* mean dihedral angles for the predominant *gauche* rotamer of the α -arylsulfonyl-*p*-substituted acetophenones^[10] **4, 7** and **1** whose values are 94° and –60°, respectively. Consequently, it became of interest to compare the IR *cis-gauche* rotamer populations of compounds **1–8** (Table I), estimated from the ratios of the absorbances at the absorption maxima of two or three components of the carbonyl band (α_c/α_g), assuming equality of the molar absorption coefficients of the two or three ro-

TABLE I Frequencies and intensity ratios of the carbonyl stretching bands in the infrared spectra of the α -arylsulfonyl-*p*-substituted acetophenones X- ϕ -C(O)-CH₂-SO₂- ϕ -Y (1–8) and the frequencies of the reference *p*-substituted acetophenones (9–11).

Compd.	X	Y	Conf. ^a	CCl ₄			CHCl ₃			CH ₃ CN		
				ν^b	α_c/α_s^c	ν^d	α_c/α_s^c	ν	α_c/α_s^c	ν	α_c/α_s^c	
1	NO ₂	OMe	c	1705.7	0.07	3375.0	0.29	1706.6	0.11	1704.8	0.18	
			g ₂	1690.7		3361.8		1690.6		1692.7		
2	NO ₂	H	c	1708.7	0.05	—	—	1707.4	0.10	1705.2	0.23	
			g ₂	1691.7		3362.0		1691.8		1693.5		
3	H	OMe	c	1701.8	0.11	3385.1	0.08	1697.1	0.22	1695.8	0.32	
			g ₁	1686.1	(0.45) ^e	3352.0	(0.74) ^e	—		—		
			g ₂	1681.5		3344.3		1680.5		1683.0		
4	H	H	c	1701.8	0.11	3385.3	(0.09)	1697.8	0.22	1695.9	0.30	
			g ₁	1687.2	(0.39) ^e	3356.4	(0.43) ^e	1686.1	(0.13) ^e	1686.1	(0.22) ^e	
			g ₂	1682.1		3345.6	—	1680.9		1683.1		
5	H	NO ₂	c	1698.0	0.11	—	—	1695.5	0.37	1695.7	0.24	
			g ₂	1680.9		—		1680.8		1684.3		
6	OMe	OMe	c	1692.5	0.05	3367.0	0.03	1688.2	0.07	1685.8	0.24	
			g ₂	1673.5		3328.9		1670.5		1673.2		
7	OMe	H	c	1692.3	0.07	3367.8	0.10	1688.1	0.11	1685.5	0.27	
			g ₂	1673.8		3330.3		1670.9		1673.3		
8	OMe	NO ₂	c	1688.4	0.13	—	—	1684.6	0.27	1684.3	0.53	
			g ₂	1672.0		—		1669.9		1673.7		
9	NO ₂	—	—	1700.5	—	—	—	1695.2	—	1696.0	—	
10	H	—	—	1691.2	—	—	—	1683.0	—	1686.1	—	
11	OMe	—	—	1683.2	—	—	—	1673.8	—	1677.3	—	

^ac, g₁, e, g₂ refers to the *cis*, *gauche*₁ and *gauche*₂ rotamers, respectively; ^bIn cm⁻¹; ^cratio of the higher and lower (or the sum of the two lower) frequency components of the analytically resolved carbonyl band; ^d1st overtone; ^eRatio of the absorbances of the middle and the lowest frequency components of the triplet; ^fIt was not possible to observe the 1st overtone bands due to the very low solubility of this compound in CCl₄.

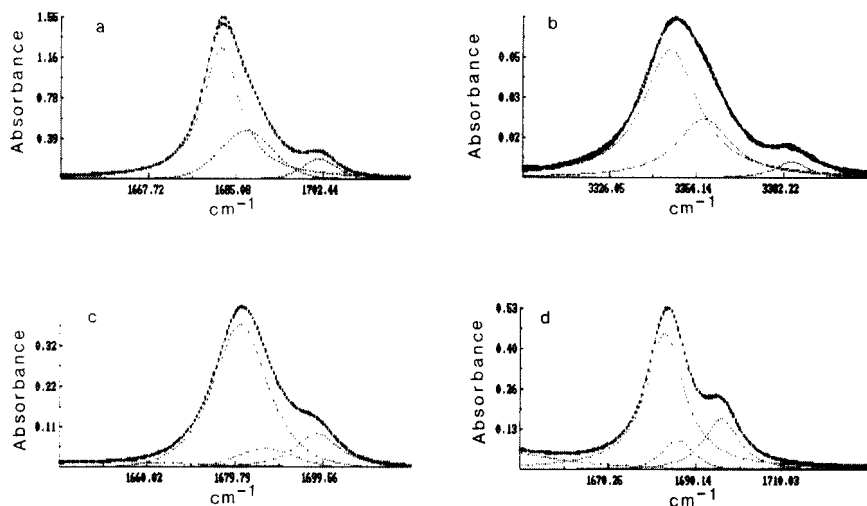


FIGURE 2 IR spectra of phenylsulfonylacetophenone (4) showing the analytically resolved carbonyl stretching bands, in carbon tetrachloride (fundamental (a) and 1st overtone (b)), chloroform (c), and acetonitrile (d).

tamers, with those obtained by MMC (Table II) for the α -methylsulfonylacetophenone. This comparison led to the following conclusions.

Firstly, the mean *gauche* rotamer concentration (*ca.* 90%) for compounds **1–8** estimated from the carbonyl band intensities (in carbon tetrachloride) is very similar to that obtained by MMC for the model compound α -methylsulfonylacetophenone ($\approx 92\%$). Secondly, the MMC data show that besides the most stable *gauche*₂ (*g*₂) rotamer, there is another less stable *gauche*₁ (*g*₁) rotamer (*c* $\approx 4.8\%$) followed by a single even less stable *cis* (*c*) rotamer (*c* $\approx 3.0\%$),

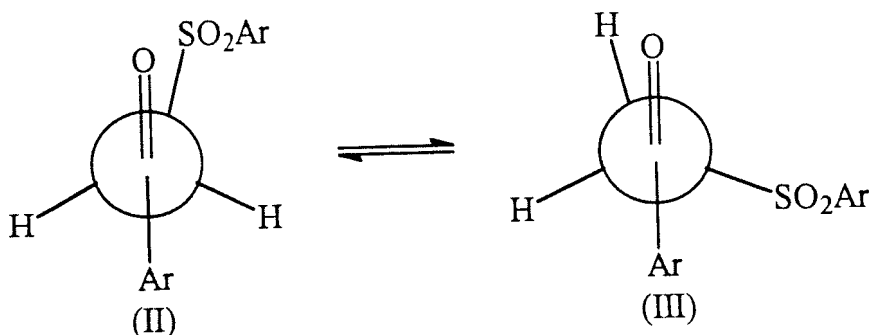


FIGURE 3 *Cis* (II) and *gauche* (III) conformations for the α -(arylsulfonyl)-*p*-substituted acetophenones.

TABLE II Calculated Molecular-Mechanics energies,^a electric dipole moments and dihedral angles for the minimum energy conformations, and the rotamers relative populations of α -methylsulfonylacetophenone $\phi\text{C}(\text{O})\text{CH}_2\text{SO}_2\text{Me}$.

Conf. ^b	θ^c	ϕ^d	$\mu^{e,f}$	E^g	P^h
c	9	-60	6.714	8.45	3.0
g_1	97	-179	6.534	7.32	4.8
g_2	91	-60	3.815	0	91.6
	(94) ⁱ	(-60) ⁱ			

^aFrom ref. [7].

^bc, g_1 and g_2 , refers to the *cis*, *gauche*₁ and *gauche*₂ conformations respectively;

^{c,d}Dihedral angles θ and ϕ (in degrees as defined in Structure IV, Figure 4);

^eIn Debye;

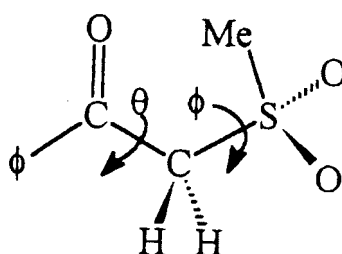
^fCalculated in benzene (From ref. [4]);

^gIn KJ mol⁻¹;

^hMolar fraction of each rotamer express in percentage;

ⁱMean dihedral angle value for the predominant *gauche* conformer of compounds **1**, **4** and **7** obtained from *ab-initio* 3-21G* calculations (From ref. [10]).

and that both g_1 as c rotamers are more polar than the g_2 rotamer. Structures V, VI and VII (Figure 5) exhibit the α -arylsulfonyl-*p*-substituted acetophenones c , g_1 and g_2 rotamers geometries, respectively, by analogy to the corresponding α -methylsulfonylacetophenone ones. Therefore from the polarity of each rotamer obtained by MMC, it is now possible to make a more precise rotamer attribution for the two or three carbonyl frequency components for compounds **1–8** presented in Table I based on the solvent effect on them. The highest frequency component of the carbonyl doublet or triplet should correspond to the most polar c rotamer; the middle component of the triplet to the more polar g_1 rotamer [compounds **3** (in CCl₄) and **4** (in all solvents)]; and the lowest frequency component of the doublet or triplet to the less polar g_2 rotamer. In fact the data for compound **4** (see Figure 2 and Table I) show that on going from



(IV)

FIGURE 4 Reference conformation ($\theta = 0^\circ$, $\phi = 0^\circ$) for the methylsulfonylacetophenone. The arrows indicate positive torsion angles.

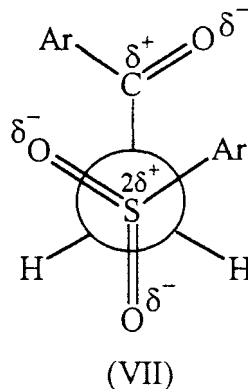
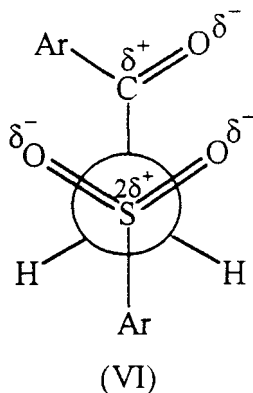
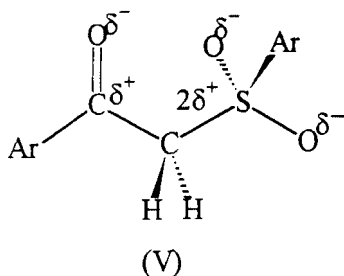


FIGURE 5 More stable conformations for the *cis*, *gauche*₁ and *gauche*₂ rotamers (structures V, VI and VII, respectively) for the α -(arylsulfonyl)-*p*-substituted acetophenones in analogy to the conformations of the α -methylsulfonylacetophenone obtained by Molecular Mechanics Calculations.

the non polar solvent carbon tetrachloride to the polar ones, chloroform and acetonitrile, there is an increase of the intensity of the highest frequency component which corresponds to the most polar *cis* (c) rotamer with the simultaneous decrease of the intensities of the middle and the lowest frequency components, which corresponds respectively to the progressive less polar *gauche*₁ (*g*₁) and *gauche*₂ (*g*₂) rotamers. As for compound **3** on going from carbon tetrachloride to chloroform and acetonitrile there is the disappearance of the middle triplet frequency component which corresponds to the less polar *g*₁ rotamer and the decrease of the intensity of the even less polar *g*₂ rotamer with the simultaneous increase of the most polar *cis* rotamer. For compounds **1**, **2**,

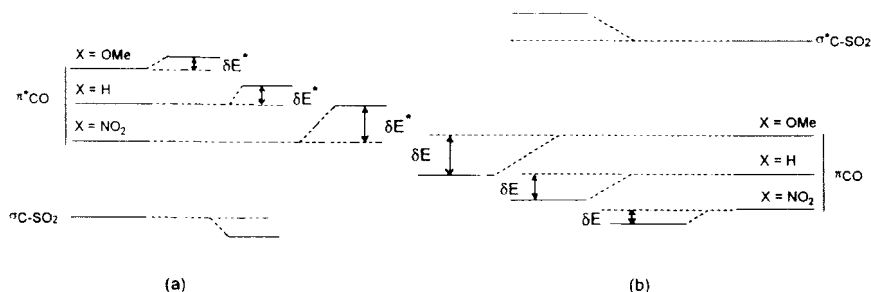


FIGURE 6 Qualitative energy level diagram showing the $\pi^*_{CO}/\sigma_{C-SO_2}$ (a) and $\pi_{CO}/\sigma^*_{C-SO_2}$ (b) orbital interactions for the *gauche* rotamers of the α -(arylsulfonyl)-*p*-substituted acetophenones varying X for the same Y substituent.

5–8 on going from carbon tetrachloride to chloroform and acetonitrile the highest doublet frequency component which corresponds to the most polar *cis* rotamer increases its intensity in detriment of the less polar *gauche*₂ rotamer, as expected. It should be pointed out that the middle frequency component which corresponds to the *g*₁ rotamer is absent for these compounds. Further support for these assignments is given by the carbonyl frequency shifts analyses (see next section).

A close inspection of Table I shows that for each acetophenone series **1**, **3**, **6**; **2**, **4**, **7** and **5**, **8** varying X from NO₂ to H and OMe for a fixed Y, there is a small but a consistent decrease of the *cis/gauche* ratio for X = NO₂ and OMe in relation to X = H. This trend indicates that within each series the *gauche* rotamer is slightly more stable when X = NO₂ and OMe in comparison with X = H.

This behavior is in agreement with our previous study on aliphatic β -keto-sulfones,^[12] which had indicated that both $\pi^*_{CO}/\sigma_{C-SO_2}$ and $\pi_{CO}/\sigma^*_{C-SO_2}$ orbital interactions, acting in opposite directions, contribute almost to the same extent for the stabilization of the *gauche* rotamers, as illustrated by Figure 6.

Figure 6(a) shows that the π^*_{CO} energy level, which is related to the LUMO of the phenacyl group, in the *p*-substituted acetophenones, decreases progressively on going from electron-donating (MeO) to electron-attracting (NO₂) substituents.^[14,15] This trend leads to a strong $\pi^*_{CO}/\sigma_{C-SO_2}$ interaction, which increases as the π^*_{CO} and σ_{C-SO_2} orbitals approximate to each other. In opposition, the $\pi_{CO}/\sigma^*_{C-SO_2}$ orbital interaction is favored on going from an electron-attracting (X = NO₂) to an electron-donating (X = OMe) substituent [Figure 6(b)]. In fact, an electron-donating substituent pushes up the π_{CO} orbital energy level, which is related to the HOMO of the phenacyl group^[5,14,15] approximating it to the $\sigma^*_{C-SO_2}$ orbital level, and thus increasing the $\pi_{CO}/\sigma^*_{C-SO_2}$ interaction, while an

electron-attracting substituent stabilizes the π_{CO} orbital level making the $\pi_{\text{CO}}/\sigma^*_{\text{C-SO}_2}$ orbital interaction more difficult.

Therefore the $\pi^*_{\text{CO}}/\sigma_{\text{C-SO}_2}$ interaction prevails over the $\pi_{\text{CO}}/\sigma^*_{\text{C-SO}_2}$ when at the phenacyl group there is an electron-attracting substituent, and a reversal behavior is observed for an electron-donating substituent leading to the predominance of the $\pi_{\text{CO}}/\sigma^*_{\text{C-SO}_2}$ orbital interaction over the $\pi^*_{\text{CO}}/\sigma_{\text{C-SO}_2}$ one.

Thus it may be concluded that the summing up of both $\pi^*_{\text{CO}}/\sigma_{\text{C-SO}_2}$ and $\pi_{\text{CO}}/\sigma^*_{\text{C-SO}_2}$ orbital interactions stabilize the *gauche* rotamers practically to the same extent when either the *para*-substituent (X) at the phenacyl group is an electron-attracting (NO_2) or an electron-donating (OMe) group, for the same Y substituent at the phenylsulfonyl group. However the slight decrease of the *gauche* rotamer stability when X = H (see Table I) suggests that in this case the summing up of $\pi^*_{\text{CO}}/\sigma_{\text{C-SO}_2}$ and $\pi_{\text{CO}}/\sigma^*_{\text{C-SO}_2}$ interactions is slightly smaller than that observed in the extremes of the series *i.e.* X = NO_2 and OMe.

Table I also shows that in the acetophenone series **8–6** (X = OMe and Y varying from NO_2 to H and OMe) there is a progressive decrease in the *cis/gauche* ratio, in the three solvents, due to the progressive stabilization of the *gauche* rotamer on going from the electron-attracting (NO_2) to hydrogen and to electron-donating (OMe) substituents. Moreover the variation of the *gauche* rotamer population in this direction is more pronounced in the polar solvents chloroform (79 to 93%) and acetonitrile (65 to 81%), than in the non polar solvent carbon tetrachloride (88 to 95%).

It should be expected that both the unperturbed $\sigma^*_{\text{C-S}}$ and $\sigma_{\text{C-S}}$ orbitals are stabilized or destabilized, when the *para*-substituent Y at the phenylsulfonyl group of the parent *p*-substituted methylphenylsulfone is an electron-attracting or an electron-donating substituent, respectively, for the same unperturbed π_{CO} or π^*_{CO} orbital energy levels of the parent *p*-substituted acetophenone, bearing at the *para* position a fixed X-substituent. Thus, the $\pi^*_{\text{CO}}/\sigma_{\text{C-SO}_2}$ and $\pi_{\text{CO}}/\sigma^*_{\text{C-SO}_2}$ orbital interactions should follow opposite trends as shown in Figure 7. Therefore, when Y = OMe, the $\pi^*_{\text{CO}}/\sigma_{\text{C-SO}_2}$ interaction reaches its maximum value, while the $\pi_{\text{CO}}/\sigma^*_{\text{C-SO}_2}$ interaction has the minimum one. On the other hand, when Y = NO_2 an opposite behavior is observed. Therefore, the summing up of $\pi^*_{\text{CO}}/\sigma_{\text{C-SO}_2}$ and $\pi_{\text{CO}}/\sigma^*_{\text{C-SO}_2}$ interactions should stabilize the *gauche* rotamers in a similar extent when the *para* substituent at the phenylsulfonyl group (Y) varies from NO_2 to H and OMe, for a fixed X (OMe). However, this expected behavior does not explain the observed progressive stabilization of the *gauche* rotamers for this series (**8–6**; Table I).

According to our previous work^[10] the observed stabilization can be mainly ascribed to the predominance of the $\text{O}_{(\text{SO}_2)} \rightarrow \text{C}_{(\text{CO})}$ electrostatic and CT interactions over the $\text{O}_{(\text{CO})} \rightarrow \text{S}_{(\text{SO}_2)}$ interaction, which occur in the *gauche* rotamers

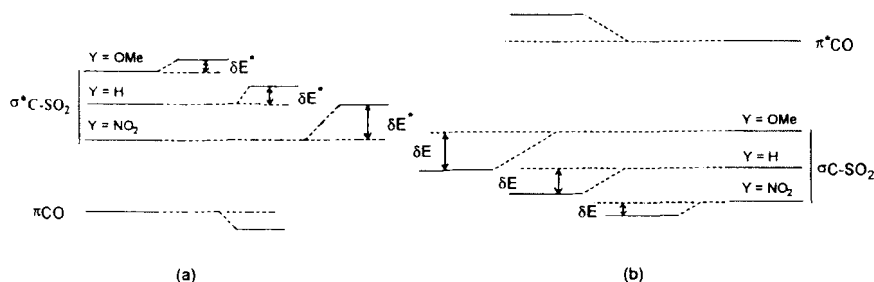


FIGURE 7 Qualitative energy level diagram showing the $\pi_{\text{CO}}/\sigma^*_{\text{C-SO}_2}$ (a) and $\pi^*_{\text{CO}}/\sigma_{\text{C-SO}_2}$ (b) orbital interactions for the *gauche* rotamers of the α -(arylsulfonyl)-*p*-substituted acetophenones varying Y for the same X substituent.

of the β -ketosulfones (Figure 8, Structure VIII). In fact, in the case of α -aryl-sulfonyl-*p*-substituted acetophenones^[10] **7**, **4** and **1** one of the oxygen atoms of the SO_2 group points towards the oppositely charged carbonyl carbon atom, both spaced by a distance slightly smaller than the sum of the van der Waals radii, and thus a significant electrostatic interaction, coupled with a small ground state charge transfer between the oxygen and carbon atoms occurs. Therefore, it seems reasonable to admit for the whole α -arylsulfonylacetophenones series **1–8** that for an electron-donating substituent ($\text{Y} = \text{OMe}$) there is an increase in the electron density on the sulfonyl oxygen atom close to the positively charged carbonyl carbon, which facilitates the $\text{O}_{(\text{SO}_2)} \rightarrow \text{C}_{(\text{CO})}$ interaction, stabilizing the *gauche* rotamer. On the other hand, for an electron attracting substituent ($\text{Y} = \text{NO}_2$) there is a decrease in the sulfonyl oxygen electron density, which leads to a stabilization of the *gauche* rotamer into a lesser extent.

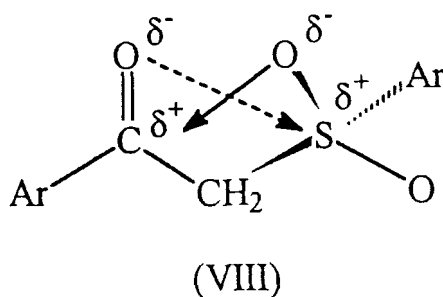


FIGURE 8 *Gauche* conformation of the (arylsulfonyl)-*p*-substituted acetophenones showing the crossed electrostatic and charge transfer interactions between the sulfonyl oxygen and the carbonyl carbon atoms (stronger interaction) and between the carbonyl oxygen and the sulfonyl sulfur atom (weaker interaction).

TABLE III Carbonyl frequency shifts^{a,b} for the *cis* ($\Delta\nu_c$) and *gauche* ($\Delta\nu_g$) rotamers of the α -(arylsulfonyl)-*p*-substituted acetophenones X- ϕ -C(O)-CH₂-SO₂- ϕ -Y.

Compound	X	Y	$\Delta\nu_c$	$\Delta\nu_g$
1	NO ₂	OMe	+5.2	-9.8
2	NO ₂	H	+8.2	-8.8
3	H	OMe	+10.6	-5.1
				-9.7
4	H	H	+10.6	-4.0
				-9.1
5	H	NO ₂	+6.8	-10.3
6	OMe	OMe	+9.3	-9.7
7	OMe	H	+9.1	-9.4
8	OMe	NO ₂	+5.2	-11.2

^aIn CCl₄.^b $\Delta\nu_c$ and $\Delta\nu_g$ refers to the difference: $\nu_{(X-\phi-C(O)-CH_2-SO_2-\phi-Y)} - \nu_{(X-\phi-C(O)-CH_3)}$, in cm⁻¹.

Similar trends are also observed, but into a minor extent, for the other two series **5–3** (X = H) and **2, 1** (X = NO₂), to which the above rationalization can be applied.

It should be pointed out that the very regular trend of the stabilization of the *gauche* rotamer in series **8–6** in comparison with the non-uniform trend in series **5–3** and **2, 1** can be rationalized as follows.

The computed MINDO/3 carbonyl carbon charges (q_c) for the parent acetophenones X- ϕ -C(O)CH₃,^[16] increases progressively from X = NO₂ (q_c = +0.602) to X = H (q_c = +0.611) and X = OMe (q_c = +0.628). Therefore stronger O_(SO₂) → C_(CO) electrostatic and charge transfer interactions should be expected in the *gauche* rotamers of the α -arylsulfonyl-*p*-substituted acetophenones when X = OMe in comparison to X = H and X = NO₂. Consequently the stabilization of the *gauche* rotamers of the *p*-methoxyacetophenone **8–6** derivatives should be affected by the variation of the Y substituent, in the phenylsulfonyl moiety, in a greater extent than it does with the *gauche* rotamers of the acetophenone **5–3** and *p*-nitroacetophenone, **2, 1** derivatives.

Carbonyl Stretching Frequency Shifts

The carbonyl frequency shifts ($\Delta\nu$) for the *cis* and *gauche* rotamers of the α -(*p*-phenylsulfonyl)-*p*-substituted acetophenones X- ϕ -C(O)CH₂SO₂- ϕ -Y **1–8**, in relation to the corresponding *p*-substituted acetophenones **9–11** (Table I), in carbon tetrachloride, are presented in Table III.

The carbonyl frequency shifts for the *cis* rotamers ($\Delta\nu_c$) are always positive while those for the *gauche* rotamers ($\Delta\nu_{g2}$) (for **1–8**) and ($\Delta\nu_{g1}$) (for **3** and **4**) are negative.

The positive *cis* shifts ($\Delta\nu_c$) support the fact that the geometry for the *cis* rotamer of the title compounds is very similar to that of the α -methylsulfonylacetophenone obtained^[4] by MMC (Structure V, Figure 5). This structure shows that the oxygen atoms of the C = O and S = O dipoles are close to each other, originating a significant Repulsive Field Effect^[12b] between them, which results in the increase of the carbonyl bond order and consequently in the ν_{CO} frequency of compounds **1–8** *cis* rotamer.

Compounds bearing the *nitro* substituent at the *para* position either of the phenacyl or of the phenylsulfonyl group, *i.e.* **1**, **2**, **5** and **8**, exhibit smaller *cis* shifts (Table III), which may be ascribed to a decrease of the polarization of the C = O or S = O dipoles, due to the electron-attracting effect of the nitro group, and leading to a smaller Repulsive Field Effect between both dipoles.

The negative *gauche* shifts ($\Delta\nu_g$) for the compounds **1–8** are in agreement with the simultaneous occurrence of both $\pi^*_{CO}/\sigma_{C-SO_2}$ and $\pi_{CO}/\sigma^*_{C-SO_2}$ interactions along with the $O_{(SO_2)} \rightarrow C_{(CO)}$ interaction, which prevail over the strong -I effect of the arylsulfonyl group [$\sigma_I(SO_2\phi) = 0.57$].^[17] leading consequently to a decrease of the carbonyl bond order and thus in the ν_{CO} frequencies for the *gauche* rotamers of the whole series (**1–8**), in relation to the corresponding parent acetophenones **9–11**.

The fact that the ($\Delta\nu_{g_2}$) shifts for compounds **3** and **4** are twice more negative than the ($\Delta\nu_{g_1}$) shifts strongly supports g_2 and g_1 geometries (Structures VII and VI, respectively; Figure 5), which are very close to the g_2 and g_1 geometries of α -methylsulfonylacetophenone obtained by MMC. In fact both the g_2 and g_1 rotamers display geometries where one of the negatively charged sulfonyl oxygen atoms point towards the positively charged carbonyl carbon atom. Thus, besides the $\pi^*_{CO}/\sigma_{C-SO_2}$ and the $\pi_{CO}/\sigma^*_{C-SO_2}$ interactions which operate in the g_1 and g_2 conformations, a $O_{(SO_2)} \rightarrow C_{(CO)}$ interaction also takes place leading to a large stabilization of the *gauche* rotamers and to a decrease of the ν_{CO} frequencies as explained above. However, in the g_1 rotamer (Structure VI) there is also a negatively charged sulfonyl oxygen atom very close to the negatively charged carbonyl oxygen atom. This proximity originates a Repulsive Field Effect between them, leading to a destabilization of g_1 in relation to g_2 conformation. This effect is also responsible for the smaller decrease of the ν_{CO} frequency of the g_1 , in relation to the g_2 rotamer which leads to a smaller negative *gauche* shift for g_1 ($\Delta\nu_{g_1}$) in relation to that for g_2 rotamer ($\Delta\nu_{g_2}$) (see Table III).

Moreover, Table I shows that the g_1/g_2 ratios for compounds **3** and **4** are always significantly smaller than **1**, which means that the g_1 rotamers are in fact less stable than the g_2 rotamers.

TABLE IV Infrared stretching^a frequencies of SO₂ group in α -(arylsulfonyl)-*p*-substituted acetophenones X- ϕ -C(O)-CH₃-SO₂- ϕ -Y (**1–8**) and in *p*-phenylsulfonylmethane derivatives Y- ϕ -SO₂-CH₃ (**12–14**).

Compd.	X	Y	CCl ₄		CHCl ₃	
			ν_{as}	ν_s	ν_{as}	ν_s
1	NO ₂	OMe	1337.02	1154.61	1330.71	1151.55
3	H	OMe	1334.32	1154.14	1328.68	1151.14
6	OMe	OMe	1333.12	1154.50	1327.57	1151.35
2	NO ₂	H	1332.63	1161.66	1329.38	1159.22
4	H	H	1330.98	1160.40	1327.59	1157.78
7	OMe	H	1330.09	1160.08	1325.41	1157.27
5	H	NO ₂	1345.24	1162.29	1346.23	1159.98
8	OMe	NO ₂	1344.71	1161.08	1340.09	1159.47
12	–	OMe	1326.98	1150.51	1319.69	1146.26
13	–	H	1326.04	1157.66	1317.82	1153.29
14	–	NO ₂	1338.62	1160.04	1330.06	1156.53

^aIn cm⁻¹.

The practically constant *gauche* shifts for the g_2 rotamers ($\Delta\nu_{g_2}$) in the whole series and for the g_1 ($\Delta\nu_{g_1}$) rotamers for compounds **3** and **4** (Table III) are in line with the almost constant summing up of the $\pi^*_{CO}/\sigma_{C-SO_2}$ and $\pi_{CO}/\sigma^*_{C-SO_2}$ orbital interactions and with the quasi-invariability of the *cis/gauche* ratios for the β -ketosulfones when X varies and Y is fixed (see preceding session).

Sulfonyl Stretching Frequencies

The sulfonyl asymmetric (ν_{as}) and symmetric (ν_s) stretching frequencies for the α -(*p*-phenylsulfonyl)-*p*-substituted acetophenones **1–8** and for the parent *p*-phenylsulfonylmethanes **12–14**, in carbon tetrachloride and chloroform, are presented in Table IV. It can be observed that the symmetric ν_{SO_2} frequencies for each acetophenone series in both solvents are nearly constant, when X changes from an electron-donating (OMe) to an electron-attracting (NO₂) substituent for a fixed Y, while there is a progressive increase of the asymmetric ν_{SO_2} frequencies, which may result from the progressive increase of the S = O bond order in the SO₂ group. Moreover there is a lowering of both (ν_{as}) and (ν_s) sulfonyl frequencies for the title compounds on going from carbon tetrachloride to chloroform. The larger solvation of the sulfonyl oxygen atoms, by the polar protic solvent (CHCl₃) in relation to the apolar one (CCl₄), is also responsible for the decrease of the S = O bond order and thus in the (ν_s) and (ν_{as}) frequencies.

Table IV also presents the sulfonyl asymmetric frequency shifts of α -arylsulfonyl-*p*-substituted acetophenones **1–8** in relation to the corresponding parent compounds **12–14**. It shows that the sulfonyl asymmetric frequency shifts

$\Delta\nu_{\text{SO}_2}(\text{as})$ for the whole series, in both solvents, are positive. These positive values can be ascribed to the inductive effect of the phenacyl group ($\sigma_{\text{I(PhCO)}} = 0.30$),^[18] which increases the S = O force constant of the SO₂ group in the arylsulfonyl moiety of compounds **1–8**. As it is also expected, the $\Delta\nu_{\text{SO}_2}(\text{as})$ values increase progressively within each acetophenone series following the σ_p parameters,^[18] when X varies from electron-donating to electron-attracting substituent for the same Y.

It should be pointed out that when X is fixed and Y changes from an electron-attracting (NO₂) to an electron-donating (OMe) substituent (series **8–6**, **5–3** and **2–1**) there are, within each acetophenone series, nearly constant $\Delta\nu_{\text{SO}_2}(\text{as})$ values in carbon tetrachloride solutions. However, there is a progressive decrease of the $\Delta\nu_{\text{SO}_2}(\text{as})$ in chloroform solutions, for the referred direction. This trend gives further support for the progressive stabilization of the *gauche* rotamer in each acetophenone series, when X is fixed and Y varies from electron-attracting to electron-donating substituents (see Table I). In fact, there is a larger solvation of the carbonyl oxygen atom in chloroform than in carbon tetrachloride, originating an increase of the formal positive charge at the carbonyl carbon atom, which in its turn should lead to a stronger electrostatic and charge transfer interactions between one of the negatively charged sulfonyl oxygen atoms and the carbonyl carbon atom in the *gauche* rotamer (Structure VIII, Figure 8), and thus these interactions shall be more pronounced for Y = OMe than for Y = NO₂.

¹³C NMR Spectroscopy

Table V shows the ¹³C NMR data for the methylene and carbonyl carbons (in -COCH₂- fragment), of the α -(*p*-phenylsulfonyl)-*p*-substituted acetophenones **1–8**, and the corresponding Non Additivity Effects^[19] (NAE), *i.e.* the differences between experimental and calculated α -methylene chemical shifts.

It is well known that the variation in conjugation involving the carbonyl group in the *p*-substituted aromatic ketones^[20] does not affect significantly the shielding on the carbonyl carbon. In fact, the β -ketosulfones **1–8** exhibit a rather constant carbonyl carbon chemical shift of *ca.* 187 ppm (Table V), *ca.* 3.0 ppm upfield in relation to the corresponding β -ketosulfoxides^[21] (X- ϕ -C(O)-CH₂-S(O) ϕ Y) carbonyl carbon chemical shifts (*ca.* 190 ppm), which cannot be simply attributed to the slightly larger inductive effect of the arylsulfonyl substituent ($\sigma_{\text{I(}\phi\text{-SO}_2\text{)}} = 0.57$)^[17] in relation to the arylsulfinyl substituent ($\sigma_{\text{I(}\phi\text{-SO)}} = 0.52$).^[17]

The computed α -methylene carbon chemical shifts^[22] for the α -arylsulfonyl-*p*-substituted acetophenones were obtained through Equation 1, where α_{Z} , and

TABLE V ^{13}C NMR chemical shifts^a for the carbonyl and α -methylene carbons (in $-\text{C}(\text{O})-\text{CH}_2-$) of α -(arylsulfonyl)-*p*-substituted acetophenones $\text{X}-\phi-\text{C}(\text{O})-\text{CH}_2\text{SO}_2\phi-\text{Y}$, in CDCl_3 .

<i>X</i>	<i>Y</i>	<i>Compd.</i>	δ_{CO}	δ_{CH_2}	$\Delta\delta_{\text{CH}_2}^b$
NO_2	OMe	1	187.06	64.11 73.69 ^c	-9.58
NO_2	H	2	186.76	63.85 73.38	-9.53
H	OMe	3	188.17	63.60 73.32	-9.72
H	H	4	187.83	63.20 73.01	-9.81
H	NO_2	5	187.49	62.84 72.80	-9.96
OMe	OMe	6	186.30	63.46 73.02	-9.56
OMe	H	7	185.89	63.18 72.71	-9.53
OMe	NO_2	8	185.84	63.02 72.50	-9.48

^aIn ppm relative to TMS; ^b $\Delta\delta = \delta_{\text{exp}} - \delta_{\text{calc}}$; ^cThe second entries are those calculated using substituent chemical shifts.

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.

$$\delta_{\text{CH}_2} = -2.3 + \alpha_{Z_1} + \alpha_{Z_2} \quad (1)$$

The α_Z effect of Z_1 and Z_2 substituents were estimated from Equation 2, *i.e.* from the chemical shifts of the methyl carbon for the $\text{H}_3\text{C}-\text{Z}$ molecules presented in Table VI and from the chemical shift of methane carbon atom.

$$\alpha_Z = \delta_{\text{CH}_3}(\text{H}_3\text{C}-\text{Z}) - \delta_{\text{CH}_4} \quad (2)$$

For instance, the calculated δ_{CH_2} for α -(*p*-methoxyphenylsulfonyl)-*p*-nitroacetophenone **1** is:

TABLE VI ^{13}C NMR chemical shifts for the methyl carbons^a of $\text{H}_3\text{C}-\text{Z}$ in CDCl_3 and α effect of the Z group (α_Z).

$\text{H}_3\text{C}-\text{Z}$	<i>Z</i>	δ_{CH_3}	α_Z
$\text{H}_3\text{C}-\text{C}(\text{O})-\phi-\text{NO}_2$	$-\text{C}(\text{O})-\phi-\text{NO}_2$	26.78	29.08
$\text{H}_3\text{C}-\text{C}(\text{O})-\phi$	$-\text{C}(\text{O})-\phi$	26.41	28.71
$\text{H}_3\text{C}-\text{C}(\text{O})-\phi-\text{OMe}$	$-\text{C}(\text{O})-\phi-\text{OMe}$	26.11	28.41
$\text{H}_3\text{C}-\text{S}(\text{O})_2-\phi-\text{NO}_2$	$-\text{S}(\text{O})_2-\phi-\text{NO}_2$	44.09	46.39
$\text{H}_3\text{C}-\text{S}(\text{O})_2-\phi^b$	$-\text{S}(\text{O})_2-\phi$	44.3	46.6
$\text{H}_3\text{C}-\text{S}(\text{O})_2-\phi-\text{OMe}$	$-\text{S}(\text{O})_2-\phi-\text{OMe}$	44.61	46.91

^aIn ppm relative to TMS; ^bFrom ref. [23].

$$\delta_{\text{CH}_2} = -2.3 + 29.08 + 46.91 = 73.69; \delta_{\text{CH}_2(\text{exp})} = 64.91 \text{ ppm}$$

The calculated α -methylene carbon chemical shifts for compounds **1–8** and the corresponding Non Additivity Effects^[19] are presented in Table V. The NAE mean value ($\Delta\delta$) for the α -methylene carbon of the β -ketosulfones ($\Delta\delta = 9.7$ ppm) is close to the corresponding mean value for the β -ketosulfoxides ($\Delta\delta = 6.9$ ppm)^[21] and for the β -ketosulfides ($\Delta\delta = 7.3$ ppm).^[6] These NAE values are smaller than those for the ω -iodoacetophenones ($\Delta\delta = 15.0$ ppm).^[24] This behavior is similar to that previously observed for the α -arylthioacetophenones^[6] and also suggests a decreasing contribution of the $\pi^*_{\text{CO}}/\sigma_{\text{C-SO}_2}$ for the *gauche* rotamers of the α -arylsulfonylacetophenones **1–8**, due to the simultaneous occurrence of the $\pi_{\text{CO}}/\sigma^*_{\text{C-SO}_2}$ orbital interaction, which leads to a decrease in the NAE.

Moreover, the larger NAE mean value for the α -methylene carbon chemical shift and the upfield shift for the carbonyl carbon of the β -ketosulfones, in relation to the β -ketosulfoxides, constitute an additional evidence for the occurrence of the $\text{O}_{(\text{SO}_2)} \rightarrow \text{C}_{(\text{CO})}$ charge transfer in the β -ketosulfones *gauche* rotamers (Structure VIII, Figure 8), which shall be responsible for the additional shielding of both the carbonyl and α -methylene carbons in **1–8**.

EXPERIMENTAL

Materials

All solvents for spectrometric measurements were spectrograde and were used without further purification. α -(*p*-Phenylsulfonyl)-*p*-substituted acetophenones $\text{X-}\phi\text{C(O)CH}_2\text{SO}_2\text{-}\phi\text{-Y}$ **1–8** were prepared essentially by the method of Drabowicz *et al.*^[25] *i.e.* from a methanolic solution of the corresponding α -(*p*-phenylthio)-*p*-substituted acetophenones^[6] containing selenium dioxide and hydrogen peroxide (30%) in a molar ratio of 1:1:5. The reaction was kept under reflux until the ketosulfide had reacted. After the reaction workup, pure solids were obtained from recrystallization in ethanol 95%. The physical, ^1H NMR and elemental analysis data of the obtained compounds **1–8** are presented in Table VII. The α -arylsulfonylacetophenones **1**, **2** and **6** are new compounds. Although compound **8** has already been described in the literature its melting point deviates significantly from ours. The arylsulphonylmethanes $\text{H}_3\text{C-SO}_2\phi\text{-Z}$ ($\text{Z} = \text{nitro}$,^[29] hydrogen^[30] and methoxy^[30]) were obtained by literature procedures.

TABLE VII Physical, ^1H NMR and elemental analysis data for the α -(*p*-phenylsulfonyl)-*p*-substituted acetophenones $\text{X}-\phi-\text{C}(\text{O})\text{CH}_2\text{SO}_2\phi-\text{Y}$.

Compd.	X	Y	M.P., (°C)	¹ H NMR ^a	Molecular formula	Calc.	C	H	Analysis (%)	N
1	NO ₂	OMe	139–142	8.33 (d, 2H, Ar ₁ ^b , J = 8.6Hz), 8.16 (d, 2H, Ar ₁ , J = 8.6Hz), 7.79 (d, 2H, Ar ₂ ^c , J = 8.7Hz), 7.02 (d, 2H, Ar ₂ , J = 8.7Hz), 4.77 (s, 2H, CH ₂), 3.90 (s, 3H, OCH ₃)	C ₁₅ H ₁₃ NO ₆ S	Calc. Found	53.72 53.81	3.91 3.80	4.18 4.30	
2	NO ₂	H	138–140	8.34 (d, 2H, Ar ₁ , J = 9.0Hz), 8.15 (d, 2H, Ar ₁ , J = 9.0Hz), 7.89 (d, 2H, Ar ₂ , J = 7.3Hz), 7.72 (t, 1H, Ar ₂ , J = 7.3Hz), 7.58 (t, 2H, Ar ₂ , J = 7.3Hz), 4.78 (s, 2H, CH ₂)	C ₁₄ H ₁₁ NO ₅ S	Calc. Found	55.08 53.32	3.63 3.92	4.59 4.59	
3	H	OMe	108–110 105–106 ^d	7.95 (d, 2H, Ar ₁ , J = 7.4Hz), 7.80 (d, 2H, Ar ₂ , J = 8.9Hz), 7.62 (t, 1H, Ar ₁ , J = 7.4Hz), 7.47 (t, 2H, Ar ₁ , J = 7.4Hz), 6.96 (d, 2H, Ar ₂ , J = 8.9Hz), 4.72 (s, 2H, CH ₂), 3.87 (s, 3H, OCH ₃)	C ₁₃ H ₁₁ O ₄ S	Calc. Found	62.05 61.97	4.86 4.77	—	
4	H	H	91–93 89–90 ^d 93–94 ^e	7.92 (t, 4H, Ar ₁ and Ar ₂ , J = 7.2Hz), 9.71–7.43 (m, 6H, Ar ₁ and Ar ₂), 4.74 (s, 2H, CH ₂)	C ₁₄ H ₁₂ O ₃ S	Calc. Found	64.60 64.42	4.65 4.39	—	
5	H	NO ₂	154–160 169–171 ^d 129 ^f	8.41 (d, 2H, Ar ₂ , J = 8.9Hz), 8.13 (d, 2H, Ar ₂ , J = 8.9Hz), 7.94 (d, 2H, Ar ₁ , J = 7.4Hz), 7.67 (t, 1H, Ar ₁ , J = 7.4Hz), 7.52 (t, 2H, Ar ₁ , J = 7.4Hz), 4.82 (s, 2H, CH ₂)	C ₁₄ H ₁₁ NO ₅ S	Calc. Found	55.08 54.91	3.63 3.60	4.59 4.23	

TABLE VII *continued*

Compd.	X	Y	M.P., (°C)	¹ H NMR ^a	Molecular formula	Calc.	Found	C	Analysis (%) C H N
6	OMe	OMe	110–116	7.92 (d, 2H, Ar ₁ , J = 8.8 Hz),	C ₁₆ H ₁₆ O ₅ S	Calc.	Found	59.99	5.03
				(d, 2H, Ar ₁ , J = 8.8 Hz),					
				6.97 (d, 2H, Ar ₂ , J = 8.7 Hz), 6.93					
7	OMe	H	108–111	(d, 2H, Ar ₂ , J = 8.7 Hz),	C ₁₅ H ₁₄ O ₄ S	Calc.	Found	62.05	4.86
				4.66 (s, 2H, CH ₂), 3.87					
				(s, 3H, OCH ₃),					
				3.86 (s, 3H, OCH ₃)					
				7.93 (d, 2H, Ar ₁ , J = 9.0 Hz), 7.89					
8	OMe	NO ₂	156–163	(d, 2H, Ar ₁ , J = 9.0 Hz),	C ₁₅ H ₁₃ NO ₆ S	Calc.	Found	53.73	3.91
				7.66 (d, 2H, Ar ₂ , J = 7.2 Hz), 7.54					
				(t, 2H, Ar ₂ , J = 7.2 Hz),					
				6.94 (d, 2H, Ar ₁ , J = 9.0 Hz) 4.69					
				(s, 2H, CH ₂), 3.88					
	OMe	NO ₂	258 ^f	(s, 3H, OCH ₃)	C ₁₅ H ₁₃ NO ₆ S	Calc.	Found	53.52	3.95
				8.39 (d, 2H, Ar ₂ , J = 8.7 Hz), 8.10					
				(d, 2H, Ar ₂ , J = 8.7 Hz),					
				7.92 (d, 2H, Ar ₁ , J = 8.8 Hz), 6.97					
				(d, 2H, Ar ₁ , J = 8.8 Hz),					
				4.77 (s, 2H, CH ₂), 3.90					4.05
				(s, 3H, OCH ₃)					

^a ¹H Chemical shifts in ppm relative to TMS and coupling constants in Hz, for CDCl₃ solutions; ^{b,c} Ar₁ and Ar₂ refer to the phenacyl and phenylsulfonyl groups, respectively, ^{d,e,f} From refs. [26, 27] and [28].

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 ($1800\text{--}1600\text{ cm}^{-1}$) was recorded in $2.0 \times 10^{-2}\text{ mol.dm}^{-3}$ carbon tetrachloride, chloroform and acetonitrile solutions, using a 0.519 mm NaCl cell. For the carbonyl first overtone region ($3600\text{--}3100\text{ cm}^{-1}$) spectra were obtained in $2.0 \times 10^{-2}\text{ mol.dm}^{-3}$ in carbon tetrachloride solutions using 1.00 cm quartz cell. The sulfonyl asymmetric ($1360\text{--}1300\text{ cm}^{-1}$) and symmetric ($1200\text{--}1100\text{ cm}^{-1}$) stretching regions, for the acetophenones **1–11** and arylsulphonylmethanes **12–14**, were recorded in carbon tetrachloride and chloroform solutions in the same conditions, as described above for the ν_{CO} fundamental region. The overlapped carbonyl stretching bands were computationally deconvoluted by means of a curve fitting program developed by Jones and Pitha.^[31, 32] Minor modifications were introduced^[33] by using the half-band width and the Cauchy-Gauss shape ratio as the input parameters. For evaluation of the accuracy of the band envelope fit the root mean square of the residuals (DIS) was used. All the carbonyl bands analyzed showed DIS values smaller than 0.5% transmittance units. The program was run in an IBM-PC/XT.

NMR measurements

^1H and ^{13}C NMR spectra of 0.5 mol.dm^{-3} solutions in CDCl_3 , with TMS as an internal reference, in 5 mm o.d. samples tubes were recorded at 200 MHz and 50 MHz , respectively, using a Bruker AC-200 spectrometer in the FT mode. The conditions for the ^1H NMR spectra were as follows: pulse width, $7.8\text{ }\mu\text{s}$; acquisition time, 2.7 s ; spectral with, 602.4 Hz ; pulse repetition time 0.0 s ; number of transients, 100; and number of data points, 32 K; and for the ^{13}C NMR spectra: pulse width, $2.0\text{ }\mu\text{s}$; acquisition time, 1.3 s ; spectral width 12500 Hz ; pulse repetition time, 1.7 s ; number of transients, 2000; and number of data points, 32 K. The ^{13}C NMR spectra were recorded both in the proton-noise and off-resonance decoupled modes.

Acknowledgements

The authors thank the Programa de Apoio Científico e Tecnológico (PADCT) for financial support of this research and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for a grant to P.R.O. and R.R.

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