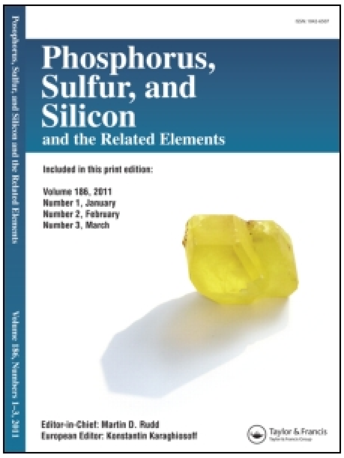

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CONFORMATIONAL AND ELECTRONIC INTERACTION STUDIES OF α-SUBSTITUTED CARBONYL COMPOUNDS. XI. ω-(*p*-PHENYLTHIO)-*p*-SUBSTITUTED ACETOPHENONES

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CONFORMATIONAL AND ELECTRONIC INTERACTION STUDIES OF α-SUBSTITUTED CARBONYL COMPOUNDS. XI. ω-(*p*-PHENYLTHIO)-*p*-SUBSTITUTED ACETOPHENONES

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The analysis of the ν_{CO} bands in the I.R. spectra of ω-(*p*-phenylthio)-*p*-substituted acetophenones indicates the presence of *cis/gauche* rotational isomerism. The decreasing *cis/gauche* ratio on going from electron-attracting to electron-donating substituents at the phenylthio group in each *p*-substituted acetophenone series is discussed in terms of the $\pi^*_{CO}/\sigma_{C\text{-}S}$ hyperconjugative interaction in the *gauche* rotamers. The carbonyl *cis* shifts ($\Delta\nu_c$) of the title compounds are interpreted as due to an interplay of Field (F) and Inductive (I) Effects. The carbonyl *gauche* shifts ($\Delta\nu_g$) trend in the whole series has been ascribed to the variation of the extension of the $\pi^*_{CO}/\sigma_{C\text{-}S}$ hyperconjugative interaction. The lower Non-Additivity Effect (NAE) of the methylene carbon of the title compounds in relation to the corresponding ω-bromo and ω-iodo acetophenones together with the lowest NAE of the methylene carbon for the ω-(*p*-nitrophenylthio)-*p*-nitroacetophenone (3) suggests the simultaneous occurrence of the $\pi^*_{CO}/\sigma_{C\text{-}S}$ and $\pi_{CO}/\sigma^*_{C\text{-}S}$ orbital interactions. The U.V. spectra of the ω-thiosubstituted acetophenones display a $n \rightarrow \pi^*_{CO}$ band which is bathochromically shifted in relation to the corresponding acetophenones except for compound (3) where this band is hypsochromically shifted. This behavior has been ascribed mainly to the $\pi^*_{CO}/\sigma^*_{C\text{-}S}$ hyperconjugative interaction in the excited state.

Key words: Conformational studies; electronic interactions; I.R. spectroscopy; ^{13}C NMR spectroscopy; U.V. spectroscopy; ω-(*p*-phenylthio)-*p*-substituted acetophenones.

INTRODUCTION

Previous reports from this laboratory on some ω-ethylthio-*p*-substituted acetophenones[1] and *p*-substituted α-phenylthioacetones[2] have suggested the existence of hyperconjugative interaction between $\pi_{CO}(\pi^*_{CO})$ and $\sigma_{C\text{-}S}(\sigma^*_{C\text{-}S})$ orbitals both in the ground and excited states as well as the occurrence of charge transfer from π_{CO} to $3d_{(S)}$ orbital in the *gauche* rotamers of such compounds. More recently our studies on ω-ethylthioacetophenone in the ω-heteroacetophenone[3] series as well as on (alkylthio)-, (alkylsulfinyl)- and (alkylsulfonyl)-propanones[4,5] have indicated the simultaneous occurrence of the $\pi^*_{CO}/\sigma_{C\text{-}S}$ and $\pi_{CO}/\sigma^*_{C\text{-}S}$ orbital interactions in the *gauche* rotamers of the title compounds.

In order to throw some more light on the nature of the above mentioned interactions which occur in 2-thiasubstituted carbonyl systems, this paper deals with I.R., ^{13}C NMR and U.V. studies of some ω-(*p*-phenylthio)-*p*-substituted acetophenones (Structure I, Figure 1) bearing at the *para* position of the phenacyl and

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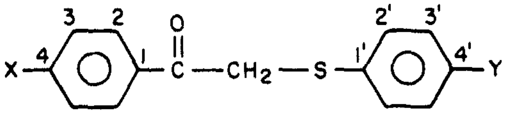


(I)

FIGURE 1 Structural formula of the ω-(*p*-phenylthio)-*p*-substituted acetophenones, being X or Y = NO_2, H and OMe substituents.

phenylthio groups electron-attracting (nitro), hydrogen and electron-donating (methoxy) substituents.

This model compound was chosen taking into account that in the *gauche* rotamers of the title compounds the $\pi_{CO}/\sigma_{C\text{-}S}$ ($\pi^*_{CO}/\sigma_{C\text{-}S}$) and $\pi_{CO}/\sigma^*_{C\text{-}S}$ orbitals interactions should be directly affected by the variations on the conjugation between the *para* substituents at the phenacyl and phenylthio groups, respectively. This, in its turn, should affect the spectroscopic properties of the title compounds.

RESULTS AND DISCUSSION

cis-gauche Rotational Isomerism

Table I shows the carbonyl stretching frequencies and the ratio of the absorbances of the higher and lower frequency components for the ω-(*p*-phenylthio)-*p*-substituted acetophenones (4), (5) and (7) in *n*-hexane, (1), (2), (4)–(9) in carbon tetrachloride (fundamental and 1st overtone transitions) and (1)–(9) in chloroform, along with the frequency data of the lower frequency component for compounds (1), (2) and (8) in *n*-hexane.

The frequency data of the single carbonyl band for the parent *p*-substituted acetophenones (10)–(12) in all solvents are included for comparison. The inspection of this Table shows that for compounds (1), (4), (5), (7) and (8) on going from non polar solvents (*n*-hexane and/or carbon tetrachloride) to a polar one (chloroform) there is an increase in the intensity of the higher frequency component in relation to the lower one except for compounds (2), (6) and (9) where the intensity ratios remain practically the same in all solvents.

Although the solvent effect[6a] on the relative intensities of the overlapped bands for the majority of the title compounds is indicative of the *cis*/*gauche* rotational isomerism, the occurrence of two overlapped carbonyl bands in the first overtone region[7] at frequencies ca. twice those in the fundamental with practically the same intensity ratios, strongly supports the *cis*/*gauche* isomerism for the whole series except for compound (3), for which a doublet is observed only in chloroform.

A good indication of the *cis*/*gauche* rotational isomerism for compound (3) is the fact that the difference between the higher and lower carbonyl frequency components (17 cm^{-1}) is practically equal to the mean value of the difference between the carbonyl stretching frequencies of the *cis* (ν_c) and the *gauche* (ν_g) conformers for the whole series, in chloroform, whose value is ca. 17 cm^{-1}.

Thus, it may be assumed for the whole series that the higher frequency band

TABLE I

Frequencies and intensities ratios of the carbonyl stretching bands in the infrared spectra of ω-(*p*-phenylthio)-*p*-substituted acetophenones X-ϕ-C(O)CH$_2$S-ϕ-Y (1)–(9) and the frequencies of the reference *p*-substituted acetophenones X-ϕ-C(O)CH$_3$ (10)–(12)

			n-C$_6$H$_{14}$		CCl$_4$				CHCl$_3$	
Compd.	X	Y	ν^{a}	α_c/α_g^{b}	ν	α_c/α_g	ν^{c}	α_c/α_g	ν	α_c/α_g
(1)	NO$_2$	OMe	–^{d} 1693	–	1710 1690	0.12	3397 3358	0.12	1709 1686	0.18
(2)	NO$_2$	H	–^{d} 1692	–	1711 1692	0.18	3396 3361	0.21	1710 1688	0.22
(3)	NO$_2$	NO$_2$	–^{e} –	–	–^{e} –	–	–^{e} –	–	1710 1693	0.35
(4)	H	OMe	1706 1687	0.14	1703 1682	0.16	3385 3345	0.17	1695 1678	0.33
(5)	H	H	1706 1688	0.20	1703 1684	0.24	3384 3346	0.20	1695 1680	0.41
(6)	H	NO$_2$	–^{e} –	–	1701 1685	0.40	3378 3346	0.34	1696 1683	0.39
(7)	OMe	OMe	1695 1680	0.14	1694 1675	0.15	3368 3330	0.16	1687 1670	0.26
(8)	OMe	H	–^{d} 1681	–	1695 1677	0.20	3368 3332	0.21	1687 1672	0.37
(9)	OMe	NO$_2$	–^{e}	–	1692 1676	0.36	3363 3334	0.36	1688 1673	0.24
(10)	NO$_2$	–	1705	–	1701	–	3376	–	1695	–
(11)	H	–	1696	–	1691	–	3358	–	1683	–
(12)	OMe	–	1690	–	1683	–	3344	–	1674	–

[a] In cm^{-1}.

[b] Ratio of the absorbances of the higher and lower frequency components of the unresolved doublet; subscripts *c* and *g* indicate *cis* and *gauche* rotamers respectively.

[c] 1st overtone.

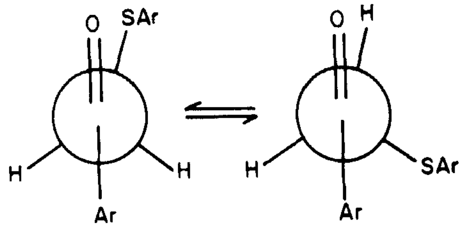
[d] The excessive noise of the band precludes the determination of the intensity of the shoulder (See Experimental Section).

[e] The compound is practically insoluble in this solvent.

corresponds to the *cis* rotamer (II) and the lower frequency band to the *gauche* rotamer (III) (Figure 2).

Due to the impossibility of determining the apparent molar absorption coefficients for the pure *cis* and *gauche* rotamers, their relative concentrations were estimated from the ratio of the absorbances directly measured at the inflexion point and at the absorption maximum of the two overlapped bands (α_c/α_g), assuming the molar absorptivities are the same for the two rotamers.

Table I also shows that for each acetophenone series O$_2$N-ϕ-C(O)CH$_2$Sϕ-Y (3)–(1); H-ϕ-C(O)CH$_2$Sϕ-Y (6)–(4) and MeO-ϕ-C(O)CH$_2$Sϕ-Y (9)–(7) bearing at the *para*-position of the phenacyl group the same substituent there is, mainly in carbon tetrachloride, a progressive decrease in the *cis*/*gauche* ratio, on going in each series from electron-attracting to electron-donating substituents at the phenylthio group. These trends have already been observed for the *p*-substituted α-



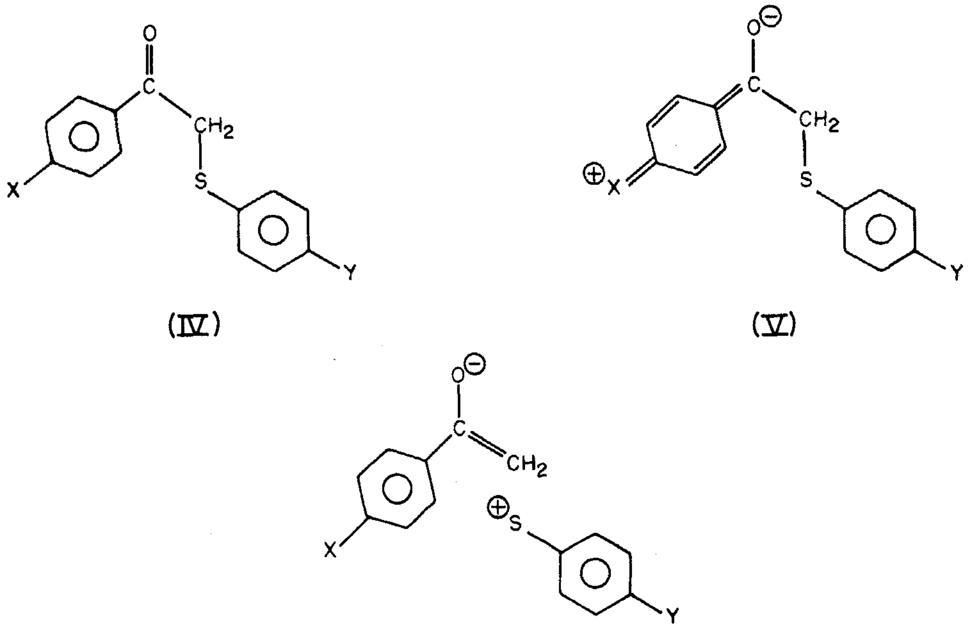
(II) (III)

FIGURE 2 *Cis* and *gauche* rotamers of ω-(*p*-phenylthio)-*p*-substituted acetophenones.

phenylthioacetones[2] and indicate a progressive stabilization of the *gauche* rotamers of the title compounds, due to the occurrence of the hyperconjugative interaction ($\pi^*_{CO}/\sigma_{C\text{-}S}$). In fact, in the case of the title compounds, in the Valence Bond theory besides the Resonance structures (IV) and (V) (Figure 3) there will be also a contribution from the hyperconjugative structure (VI) (Figure 3) that will increase on going from electron-attracting to electron-donating *para* substituents at the phenylthio group for the same *para* substituent at the phenacyl group.

Carbonyl Stretching Frequency Shifts

Table II shows the carbonyl frequency shifts ($\Delta\nu$), in chloroform, for the *cis* and *gauche* rotamers of the ω-(*p*-phenylthio)-*p*-substituted acetophenones X-



(IV) (V) (VI)

FIGURE 3 Resonance structures for the ω-(*p*-phenylthio)-*p*-substituted acetophenones.

TABLE II

Carbonyl frequency shifts[a,b] for the *cis* ($\Delta\nu_c$) and *gauche* ($\Delta\nu_g$) rotamers of ω-(*p*-phenylthio)-*p*-substituted acetophenones X-ϕ-C(O)$CH_2S\phi$-Y (1)–(9) in relation to the parent *p*-substituted acetophenones[c] X-ϕ-C(O)CH_3 (10)–(12)

Compd.	X	Y	$\Delta\nu_c$	$\Delta\nu_g$
(1)-(10)	NO_2	OMe	+14	-9
(2)-(10)	NO_2	H	+15	-7
(3)-(10)	NO_2	NO_2	+15	-2
(4)-(11)	H	OMe	+12	-5
(5)-(11)	H	H	+12	-3
(6)-(11)	H	NO_2	+13	0
(7)-(12)	OMe	OMe	+13	-4
(8)-(12)	OMe	H	+13	-2
(9)-(12)	OMe	NO_2	+14	+1

[a] In $CHCl_3$.

[b] $\Delta\nu_c$ and $\Delta\nu_g$ in cm^{-1}, refers to the difference: $\nu_{[X-\phi-C(O)CH_2S\phi-Y]} - \nu_{[X-\phi-C(O)CH_3]}$.

[c] See Table I.

ϕC(O)$CH_2S\phi$-Y (1)–(9), in relation to the corresponding *p*-substituted acetophenones X-ϕC(O)CH_3 (10)–(12). The carbonyl frequency shifts for the *cis* rotamers ($\Delta\nu_c$) are always positive (+15 to +12 cm^{-1}) whilst those for the *gauche* rotamers ($\Delta\nu_g$) vary from negative to slight positive (−9 to +1 cm^{-1}) values.

The positive *cis* shifts may be ascribed to the Repulsive Field Effect[6b,8] between the C═O and C—S dipoles combined with the inductive effect of the substituents. However, a close inspection of Table II shows that for each acetophenone series O_2N-ϕ-C(O)$CH_2S\phi$-Y (1)–(3), H-ϕ-C(O)$CH_2S\phi$-Y (4)–(6) and MeO-ϕ-C(O)$CH_2S\phi$-Y (7)–(9) bearing at the *para* position of the phenacyl group the same substituent, there is practically no variation in the carbonyl *cis* shifts on going from electron-donating to electron-attracting *para* substituents at the phenylthio group.

This trend may be explained as in the case of the *p*-substituted α-phenylthioacetones[2] by the practical cancellation of the additional Inductive Effect $-I_\sigma$ or $+I_\sigma$ and the resulting additional Attractive or Repulsive Field Effect induced respectively by the electron-attracting (NO_2) (Structure VII, Figure 4) or electron-donating (OMe) (Structure VIII, Figure 4) *para* substituents at the phenylthio group in relation to the unsubstituted phenylthio group of each acetophenone series. Thus, as a consequence of the practical invariability of the carbonyl double bond character in the two extreme cases analyzed a negligible change in the carbonyl force constant and in the ν_{CO} frequencies of the *cis* rotamers of each acetophenone series should occur. This will lead therefore to practically the same carbonyl *cis* shifts (for more details see our preceding paper[2]).

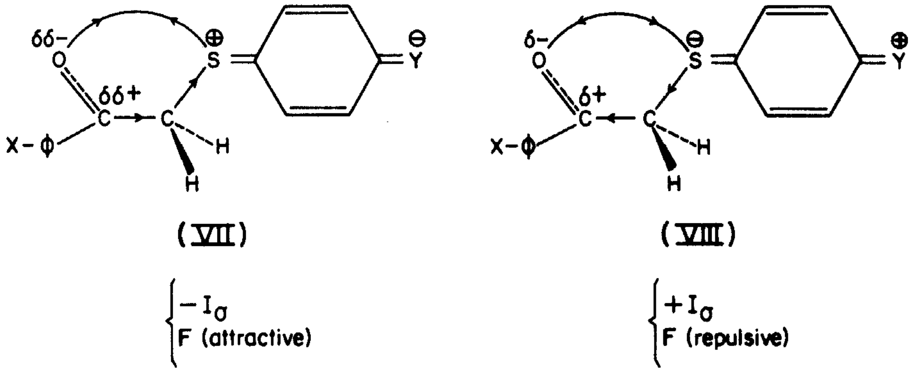


FIGURE 4 *Cis* conformers for ω-(*p*-phenylthio)-*p*-substituted acetophenones bearing at the phenacyl group the same *para* substituent (*X*) and varying the *para*-substituent at the phenylthio group (*Y*), showing the Field (*F*) and the Inductive (*I*) Effects acting in opposition in both structures.

Table II shows that for each acetophenone series bearing at the *para* position of the phenacyl group the same substituent, there is a progressive less negative carbonyl *gauche* shifts on going from (1)–(3), (4)–(6) and (7)–(9). As expected, this trend follows the normal effect of the substituents i.e. the progressive increase of the carbonyl frequency for the *gauche* rotamers of each acetophenone series as the *para* substituent at the phenylthio group changes from electron-donating (OMe) to electron-attracting (NO_2) substituents (Table I). As a consequence this will lead to the progressive less negative carbonyl *gauche* shifts for the title compounds in relation to the corresponding parent acetophenones.

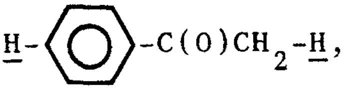
On the other hand Table II shows that when the *para* substituent at the phenylthio group is constant (*Y* = OMe or H) and the *para* substituent at the phenacyl group varies from electron-donating to electron-attracting substituents, there is a progressive increase in absolute value of the negative carbonyl frequency shifts of the *gauche* rotamers for compounds X-ϕ-C(O)CH_2Sϕ-OMe (7), (4), (1) and X-ϕ-C(O)CH_2Sϕ-H (8), (5), (2) in relation to the corresponding parent acetophenones X-ϕ-C(O)CH_3 (12), (11), (10) except for the case of the *p*-nitrophenylthio derivatives X-ϕ-C(O)CH_2Sϕ-NO_2 (9), (6), (3) where the *gauche* shifts vary from slightly positive to negative (+1 to -2 cm^{-1}) value.

As a consequence of the above trends the minor carbonyl *gauche* shift occurs for the ω-(*p*-nitrophenylthio)-*p*-methoxyacetophenone (9) ($\Delta\nu_g$ = +1 cm^{-1}) and the more negative one occurs for the ω-(*p*-methoxyphenylthio)-*p*-nitroacetophenone (1) ($\Delta\nu_g$ = -9 cm^{-1}). These results may be analysed in the light of the V.B. theory as in the case of the previously reported ω-ethylthio-*p*-substituted acetophenones[1] by the following considerations.

It is to be expected a greater contribution of the dipolar hyperconjugative structure (VI) in detriment of the Resonances structures (IV) and (V) (Figure 3), as the *para*-phenacyl substituent is more electron-attracting and the *para*-phenylthio substituent is more electron-donating. So, the large frequency shift (-9 cm^{-1}) noticed in the ω-(*p*-methoxyphenylthio)-*p*-nitroacetophenone (1) results from the decrease in the carbonyl force constant, due to a greater contribution of the hyperconjugative structure (VI).

On the other hand, it is to be expected a smaller contribution of the hyperconjugative structure (VI) in relation to the dipolar Resonance one (V) as the *para*-phenacyl substituent is more electron-donating and the *para*-phenylthio substituent is more electron-attracting. Thus, the small frequency shift ($+1$ cm^{-1}) observed in the ω-(p-nitrophenylthio)-p-methoxyacetophenone (9) is a consequence of the smaller decrease in the carbonyl force constant, due to a smaller contribution of the hyperconjugative structure (VI).

An even more straightforward analysis of the carbonyl *gauche* shifts can be performed by the comparison of carbonyl frequency shifts induced by the effects of both *para*-phenacyl (X) and *omega* - ($-S\phi Y$) substituents acting independently on the unsubstituted acetophenone molecule



and the effects of the referred substituents acting simultaneously on the acetophenone, as in the case of the ω-(p-phenylthio)-p-substituted acetophenones X-ϕC(O)CH$_2$-SϕY.

Table III shows the summing up of the carbonyl frequency shifts ($\Delta\nu_1$) of the p-substituted acetophenones X-ϕC(O)CH$_3$ (10), (12) and the carbonyl frequency shifts of the *gauche* rotamers ($\Delta\nu_2$) for the ω-(p-phenylthio)acetophenones ϕC(O)CH$_2$Sϕ-Y (4)–(6) compared with the carbonyl frequency shifts of the *gauche* rotamers ($\Delta\nu_3$) for the ω-(p-phenylthio)-p-substituted acetophenones X-ϕC(O)CH$_2$Sϕ-

TABLE III

Comparison of the summing up of the carbonyl frequency shifts[a,b] of the p-substituted acetophenones X-ϕ-C(O)CH$_3$ (10), (12) ($\Delta\nu_1$)[c] and the carbonyl frequency shifts for the *gauche* rotamers of the ω-(p-phenylthio)acetophenones ϕ-C(O)CH$_2$Sϕ-Y (4)–(6) ($\Delta\nu_2$)[d], with the carbonyl frequency shifts for the *gauche* rotamers of ω-(p-phenylthio)-p-substituted acetophenones X-ϕ-C(O)CH$_2$Sϕ-Y (1)–(3), (7)–(9) ($\Delta\nu_3$)[e]

X	Compd.	$\Delta\nu_1$	Y	Compd.	$\Delta\nu_2$	$\Delta\nu_1+\Delta\nu_2$	X	Y	Compd.	$\Delta\nu_3$
NO$_2$	(10)	+12	SϕOMe	(4)	-5	+7	NO$_2$	SϕOMe	(1)	+3
NO$_2$	(10)	+12	Sϕ	(5)	-3	+9	NO$_2$	Sϕ	(2)	+5
NO$_2$	(10)	+12	SϕNO$_2$	(6)	0	+12	NO$_2$	SϕNO$_2$	(3)	+10
OMe	(12)	-9	SϕOMe	(4)	-5	-14	OMe	SϕOMe	(7)	-13
OMe	(12)	-9	Sϕ	(5)	-3	-12	OMe	Sϕ	(8)	-11
OMe	(12)	-9	SϕNO$_2$	(6)	0	-9	OMe	SϕNO$_2$	(9)	-8

[a] In CHCl$_3$.

[b] In cm^{-1}.

[c] $\Delta\nu_1 = \nu_{[X-\phi C(O)CH_3]} - \nu_{[\phi C(O)CH_3]}$.

[d] $\Delta\nu_2 = \nu_{[\phi C(O)CH_2S\phi-Y]} - \nu_{[\phi C(O)CH_3]}$.

[e] $\Delta\nu_3 = \nu_{[X-\phi C(O)CH_2S\phi-Y]} - \nu_{[\phi C(O)CH_3]}$.

Y (1)–(9) in relation to the unsubstituted acetophenone $\phi C(O)CH_3$ (11). This Table shows that when the para-substituent at the phenacyl group is the electron-donating (OMe) group, $\Delta\nu_3$ has practically the same value of the summing up ($\Delta\nu_1$ + $\Delta\nu_2$) and when the *para*-substituent at the phenacyl group is the electron-attracting (NO_2) group, $\Delta\nu_3$ value is lower than the summing up ($\Delta\nu_1 + \Delta\nu_2$).

The above trend is in line with the carbonyl frequency shift analysis discussed above i.e. when the *para* substituent at the phenacyl group is the electron-donating (OMe) group, the strong conjugation between this group and the phenacyl group practically precludes the hyperconjugative interaction (Structure VI, Figure 3). Therefore in this case only the normal substituent effects of the (OMe) and ($-S\phi Y$) groups act on the acetophenone molecule leading practically to the same carbonyl frequency shift values for $\Delta\nu_3$ and ($\Delta\nu_1 + \Delta\nu_2$).

On the other hand when the *para* substituent at the phenacyl group is the electron-attracting (NO_2) group, the hyperconjugation (Structure VI, Figure 3) becomes more important than the conjugation between the *para* substituent and the phenacyl group. As a consequence there is besides the normal substituent effects of both (NO_2) and ($-S\phi Y$) groups acting on the acetophenone molecule, the additional hyperconjugative effect which leads to the lowering of the carbonyl frequency shifts ($\Delta\nu_3$) in relation to the ($\Delta\nu_1 + \Delta\nu_2$) values. As expected, this carbonyl frequency shift lowering is greater for the *p*-methoxyphenylthio derivative (1) due to the greater contribution of the dipolar hyperconjugative structure and minor for the *p*-nitrophenylthio derivative (3) for which the referred contribution is lower.

Carbon-13 NMR Chemical Shifts

The ^{13}C NMR chemical shifts of the aromatic carbons and of the carbonyl and methylene carbons in ($-C(O)CH_2$-group) for the ω-(*p*-phenylthio)-*p*-substituted acetophenones are shown in Tables IV and V, respectively.

The assignments of the signals of the aromatic carbons for the ω-phenylthioacetophenone $\phi C(O)CH_2S\phi$ (5) were made by comparison to the experimental chemical shifts of related molecules such as ω-ethylthioacetophenone $\phi C(O)CH_2SC_2H_5$ (13) and ethylphenylsulfide $C_2H_5S\phi$ (14) (Table IV).

The attribution of the aromatic carbons for the other ω-(*p*-phenylthio)-*p*-substituted acetophenones were made by the analysis of the relative intensities of the signals of each ring carbon atom and by matching their experimental chemical shifts with the corresponding computed chemical shifts as described below.

The chemical shifts for the aromatic carbons of the phenacyl (C-1, C-2, C-3 and C-4) and phenylthio (C-1′, C-2′, C-3′, C-4′) groups (see Structure I, Figure 1) were calculated from the substituent chemical shifts (SCS) of Ewing's[10] tabulation and for the $-C(O)CH_2S\phi$-Y (*p*) and $-SCH_2C(O)\phi$-X (*p*) groups were estimated respectively from the experimental chemical shifts of the compounds $\phi C(O)CH_2S\phi$-Y and X-$\phi C(O)CH_2S\phi$ in relation to the chemical shift of the benzene carbon (128.5 ppm). These substituents chemical shifts were presented in Table VI. For the sake of illustration, the chemical shifts of C-1 and C-1′ for the ω-(*p*-methoxyphenylthio)-*p*-nitroacetophenone (1) are calculated by following equations:

$$\delta_{C\text{-}1} = \delta_{C_6H_6} + \delta_{ipso}\,(\text{-}C(O)CH_2S\phi OMe) + \delta_{para}\,(NO_2) \tag{1}$$

$$\delta_{C\text{-}1} = 128.5 + 6.91 + 6.1 = 141.51\ \text{ppm};\ \delta_{C\text{-}1\ (exp.)} = 140.0\ \text{ppm}$$

TABLE IV

^{13}C NMR chemical shifts[a] of the aromatic carbons[b] for the ω-(*p*-phenylthio)-*p*-substituted acetophenones X-ϕ-C(O)CH$_2$-Sϕ-Y (*1*)–(*9*), ω-ethylthioacetophenone ϕC(O)CH$_2$SC$_2$H$_5$ (*13*) and ethylphenylsulfide C$_2$H$_5$Sϕ (*14*), in CDCl$_3$

	Subst.		Aromatic carbons								Other carbons	
Compd.	X	Y	C-1	C-2,6	C-3,5	C-4	C-1'	C-2',6'	C-3',5'	C-4'	C(X)	C(Y)
(1)	NO_2	OMe	140.00	129.56	123.40	150.19	123.58	134.70	114.73	159.96		55.11
			141.51[c]	129.41	123.49	152.94	125.81	130.71	116.47	158.94		
(2)	NO_2	H	139.80	129.55	123.63	150.24	133.52	129.07	130.89	127.54		
			140.89	129.36	123.56	153.07	-	-	-	-		
(3)	NO_2	NO_2[d]	144.94	126.97	123.95	150.37	140.06	130.14	123.97	146.15		
			141.08	129.33	122.33	153.76	139.62	131.79	124.17	147.44		
(4)	H	OMe	135.41	128.51	128.39	133.04	124.60	134.35	114.59	159.57		58.88
			-	-	-	-	127.72	131.44	114.44	158.29		
(5)	H	H	134.79	128.46	128.46	133.17	135.43	130.40	128.86	126.89		
			-	-	-	-	-	-	-	-		
(6)	H	NO_2	134.98	128.43	127.23	133.86	-[e]	128.79	123.77	145.23		
			-	-	-	-	141.53	131.30	123.96	146.79		
(7)	OMe	OMe	130.79	128.35	113.57	163.48	124.80	134.14	114.49	159.48	55.22	55.05
			127.70	129.55	113.97	164.44	127.35	131.80	114.37	158.13		
(8)	OMe	H	128.40	130.18	113.71	163.66	135.06	130.79	128.79	126.73	55.27	
			127.08	129.50	114.04	164.57	-	-	-	-		
(9)	OMe	NO_2	127.93	127.07	113.97	164.14	-[e]	130.83	123.78	145.59	55.39	
			127.27	129.47	112.81	165.26	141.16	131.65	123.89	146.03		
(13)	-	-[f]	135.15	128.57	128.41	133.04	-	-	-	-	26.17[g]	13.97[h]
(14)	-	-[f]	-	-	-	-	136.46	128.84	128.64	125.55	27.45[g]	14.20[h]

[a] In ppm relative to TMS.

[b] The numbering of the aromatic carbon atoms for the phenacyl and phenylthio groups are shown in Figure 1.

[c] The second entries are those calculated using substituent chemical shifts (see text).

[d] In DMSO-d_6.

[e] The signal should be lost in the noise.

[f] From ref. 9.

[g,h] Refers respectively to the methylene and methyl carbons of the ethyl group.

TABLE V

^{13}C NMR chemical shifts[a] for the carbonyl and methylene carbons (in -C(O)CH_2-) of ω-(*p*-phenylthio)-*p*-substituted acetophenones (1)–(9), in $CDCl_3$

Compd.	X	Y	δ_{CO}	δ_{CH_2}	$\Delta\delta_{CH_2}$[b]
(1)	NO_2	OMe	192.37	42.59 50.68[c]	-8.09
(2)	NO_2	H	192.29	41.18 48.56	-7.38
(3)	NO_2	NO_2[d]	192.98	40.47 47.03	-6.56
(4)	H	OMe	194.06	42.58 50.31	-7.73
(5)	H	H	193.81	41.07 48.19	-7.12
(6)	H	NO_2	192.60	39.14 46.70	-7.56
(7)	OMe	OMe	192.75	42.33 50.01	-7.68
(8)	OMe	H	192.43	40.79 47.89	-7.10
(9)	OMe	NO_2	191.10	39.85 46.40	-6.55

[a] In ppm relative to TMS.
[b] $\Delta\delta = \delta_{exp.} - \delta_{calc.}$
[c] The second entries are those calculated using substituent chemical shifts (see text).
[d] In DMSO-d_6.

$$\delta_{C\text{-}1'} = \delta_{C_6H_6} + \delta_{ipso}\,(\text{-}SCH_2C(O)\phi NO_2) + \delta_{para}\,(OMe)$$
$$\delta_{C\text{-}1'} = 128.5 + 5.02 + (-7.71) = 125.81 \text{ ppm};\ \delta_{C\text{-}1'\,(exp.)} = 123.58 \text{ ppm} \qquad (2)$$

Table IV shows that there is in general a good agreement between the experimental and the computed chemical shifts of the aromatic carbons for the ω-(*p*-phenylthio)-acetophenones series (1)–(4), (6)–(9), indicating the correct attribution of each aromatic carbon atom.

It should be pointed out that as in the case of the ω-ethylthioacetophenones[1] the mean value of the carbonyl carbon chemical shifts of the title compounds (1)–(9) (Table V) (ca. 193 ppm) is shielded by ca. 4 ppm in relation to the corresponding *p*-substituted acetophenones[1] whose mean value of the carbonyl carbon chemical shifts is ca. 197 ppm. This behavior may be ascribed to the electron-attracting inductive effect of the α-arylthio group.

The calculated[11] α-methylene carbon chemical shifts were obtained through equa-

TABLE VI

^{13}C substituents chemical shifts[a] (SCS) in monosubstituted benzenes

Substituent	δ_{ipso}	δ_{orto}	δ_{meta}	δ_{para}
NO_2[b]	19.9	-4.9	0.9	6.1
OMe[b]	31.40	-14.42	1.04	-7.71
$C(O)CH_2S\phi NO_2$[c](p)	6.48	-0.07	-1.27	5.16
$C(O)CH_2S\phi$[c]	6.29	-0.04	-0.04	4.67
$C(O)CH_2S\phi OMe$[c](p)	6.91	-0.01	-0.11	4.54
$SCH_2C(O)\phi NO_2$[d](p)	5.02	0.57	2.39	-0.96
$SCH_2C(O)\phi$[d]	6.93	1.90	0.36	-1.61
$SCH_2C(O)\phi OMe$(p)[d]	6.56	2.29	0.29	-1.77

[a] Relative to benzene.

[b] From ref. 10.

[c,d] SCS obtained from the experimental chemical shifts of carbons 1, 2, 3 and 4 for compounds (4), (5) and (6) and of carbons 1', 2', 3' and 4' for compounds (2), (5) and (8) from Table IV, respectively.

TABLE VII

^{13}C NMR chemical shifts[a] for the α-methylene or α-methyl carbon atoms of the R-Z molecules, in $CDCl_3$, and the alfa effect of the Z substituents (α_Z)

Z	R-Z	$\delta_{R\text{-}Z}$[b]	α_Z
$S\text{-}\phi\text{-}NO_2$(p)	$H_3C\text{-}\underline{CH}_2\text{-}S\phi NO_2$	25.99[c]	20.29
$S\phi$	$H_3C\text{-}\underline{CH}_2\text{-}S\phi$	27.48[c]	21.78
$S\text{-}\phi\text{-}OMe$(p)	$H_3C\text{-}\underline{CH}_2\text{-}S\phi OMe$	29.60[c]	23.90
$C(O)\text{-}\phi\text{-}NO_2$(p)	$H_3\underline{C}\text{-}C(O)\text{-}\phi NO_2$	26.78[d]	29.08
$C(O)\text{-}\phi$	$H_3\underline{C}\text{-}C(O)\phi$	26.41[d]	28.71
$C(O)\text{-}\phi\text{-}OMe$(p)	$H_3\underline{C}\text{-}C(O)\phi OMe$	26.11[d]	28.41

[a] In ppm relative to TMS.

[b] Refers to the α-methylene or methyl carbon chemical shifts.

[c] From ref. 2.

[d] From ref. 1.

tion (3), 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.

$$\delta_{CH_2} = -2.3 + \alpha_{Z_1} + \alpha_{Z_2} \tag{3}$$

The α_Z effects of Z_1 and Z_2 substituents were estimated from the chemical shifts of the α-methylene or α-methyl carbons for R-Z molecules presented in Table VII and the chemical shifts of the carbon atoms for the corresponding alcanes R—H (i.e. 5.7 ppm for ethane and −2.3 ppm for methane).

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

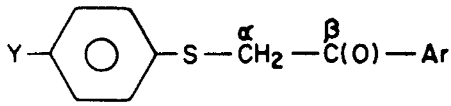
$$\delta_{CH_2} = -2.3 + 29.08 + 23.90 = 50.68 \text{ ppm}; \ \delta_{CH_2\,(exp.)} = 42.59 \text{ ppm}$$

Table V shows that when *Y* substituent is constant and *X* varies from electron-donor to electron-acceptor substituents, there is a slight progressive deshielding of the methylenic carbon. This trend is similar to that observed for the methyl carbon of the *p*-substituted acetophenones and follows the normal effect of the substituents. On the other hand when *X* is constant and *Y* varies from electron-donor to electron-attracting substituents there is a significant shielding of the methylene carbon (ca. 3 ppm). It is worth noting that the same trend but in a lesser extent can be observed for the carbonyl carbon of the title compounds.

The greater shielding effect on the α carbon atom (methylene group) in relation to the β carbon atom (carbonyl group) for the ω-(*p*-phenylthio)-*p*-substituted acetophenones (1)–(9) (Structure IX, Figure 5), on going from electron-donating to electron-attracting substituents at the *para* position of the phenylthio group is a general effect which was previously[2] observed for the *p*-substituted α-phenylthioacetones, α-phenylthioacetonitriles and α-phenylethylthioethers. This behavior may be ascribed to the Reverse Polar Effect,[12,13] being more important for the α-carbon than for the β one (for more details see our preceding paper[2]).

A comparison between the experimental and calculated α-methylene carbon chemical shifts (Table V) leads to $\Delta\delta$ values (Non-Additivity Effect), which may be ascribed as proposed by Nesmeyanov[14] to an increase in the double bond character between the α-methylene and carbonyl carbons due to the $\pi^*_{CO}/\sigma_{C\text{-}S}$ hyperconjugative interaction. In fact, the experimental chemical shifts for the α-methylene carbon for the ω-(*p*-phenylthio)-*p*-substituted acetophenones (1)–(9) are upfield shifted in relation to the calculated values by ca. 7 ppm. It should be pointed out that the higher Non-Additivity value is observed for the ω-(*p*-methoxyphenylthio)-*p*-nitroacetophenone $O_2N\text{-}\phi C(O)CH_2S\phi\text{-}OMe$ (1) (8.09 ppm) and the lower one for the ω-(*p*-nitrophenylthio)-*p*-methoxyacetophenone $MeO\text{-}\phi C(O)CH_2S\phi\text{-}NO_2$ (9) (6.55 ppm). This trend is in line with the I.R. data of the title compounds which indicate that the major contribution of the $\pi^*_{CO}/\sigma_{C\text{-}S}$ hyperconjugative interaction (Structure VI, Figure 3) is for compound (1) and the minor one is for compound (9).

It is worth mentioning that, as in the case of the ω-ethylthioacetophenones,[1] the Non-Additivity mean value for the title compounds (1)–(9) is ca. 7 ppm, being



(IX)

FIGURE 5 General structure for the *para*-substituted α-phenyl-thioacetophenones.

practically half the values for the ω-bromo and ω-iodoacetophenones[15] for which the Non-Additivity Effects are ca. 15 ppm. This behavior suggests the decreasing contribution of the hyperconjugative interaction for the *gauche* rotamers of the ω-(*p*-phenylthio)-*p*-substituted acetophenones (1)–(9), due to the simultaneous occurrence of the $\pi_{CO}/\sigma^*_{C\text{-}S}$ charge transfer leading as a consequence to a decrease in the Non-Additivity Effect for the methylene carbon of the title compounds.

A support for the close relationship between the $\pi_{CO}/\sigma^*_{C\text{-}S}$ orbitals interaction and the decreasing Non-Additivity Effect is the observed low $\Delta\delta$ value of ca. 6.6 ppm of the methylene carbon atom for the ω-(*p*-nitrophenylthio)-*p*-nitroacetophenone (3) in the whole ω-(*p*-phenylthio)acetophenone series. In fact, in this case the electron-attracting *para*-nitro substituent at the phenacyl group induces a greater electronic density of the carbonyl π orbital, facilitating therefore the charge transfer to the stabilized $\sigma^*_{C\text{-}S}$ orbital of the *p*-nitrophenylthio group. As a consequence, a decreasing on the shielding of the methylene carbon for the title compound occurs.

Carbonyl n → π Transition Energies and Intensities*

Table VIII shows the $n \rightarrow \pi^*_{CO}$ transition energies and their band intensities for the ω-(*p*-phenylthio)-*p*-substituted acetophenones (1)–(9) and the corresponding data for the *p*-substituted acetophenones (10)–(12) and ω-ethylthioacetophenones (15), (13) and (16) for comparison purpose.

Similarly to the ω-ethylthio-*p*-substituted acetophenones[1] bearing at the *para*

TABLE VIII

U.V. data for the carbonyl $n \rightarrow \pi^*$ transition of the ω-(*p*-phenylthio)-*p*-substituted acetophenones X-ϕC(O)CH$_2$Sϕ-Y (1)–(9) and of the corresponding *p*-substituted acetophenones[a] X-ϕC(O)CH$_3$ (10)–(12) and ω-(ethylthio)-*p*-substituted acetophenones[b] X-ϕC(O)CH$_2$SEt (15), (13) and (16), in *n*-hexane

Compd.	X	Y	λ[c]	ε[d]
(1)	NO_2	OMe	357[e]	977
(2)	NO_2	H	357	676
(3)	NO_2	NO_2	302[e]	3462
(4)	H	OMe	339	740
(5)	H	H	340	555
(6)	H	NO_2	320	6471
(7)	OMe	OMe	334	993
(8)	OMe	H	333	762
(9)	OMe	NO_2	322[e]	16935
(10)	NO_2	-	325[e]	288
(11)	H	-	317	43
(12)	OMe	-	310	97
(15)	NO_2	-	357	766
(13)	H	-	339	471
(16)	OMe	-	332	890

[a] From ref. 16.
[b] From ref. 1.
[c] In nm.
[d] Apparent molar absorptivity in $l.mol^{-1}.cm^{-1}$.
[e] Shoulder.

position of the phenacyl group the nitro (15), hydrogen (13) and methoxy (16) substituents the introduction of the phenylthio group containing at the *para* position the *methoxy* and *hydrogen* substituents at the ω-position of the corresponding acetophenones X-ϕC(O)$\underline{C}$H$_3$ (10)–(12) results in a bathochromic shift of the $n \rightarrow \pi^*$ transition band of ca. 32 nm for compounds O$_2$N-ϕC(O)CH$_2$Sϕ-Y (1), (2) and ca. 22 nm for compounds H-ϕC(O)CH$_2$Sϕ-Y (4), (5) and MeO-ϕC(O)CH$_2$Sϕ-Y (7), (8), followed by an hyperchromic effect. On the other hand, the introduction of the *p-nitrophenylthio* group at the ω-position of the acetophenones (10)–(12) leads to a smaller bathochromic shifts for both *p*-methoxyacetophenone MeO-ϕC(O)CH$_2$Sϕ-NO$_2$ (9) and acetophenone H-ϕC(O)CH$_2$Sϕ-NO$_2$ (6) derivatives of ca. 12 nm and 3 nm, respectively, and to a significant hypsochromic effect of ca. 23 nm for the *p*-nitroacetophenone O$_2$N-ϕC(O)CH$_2$Sϕ-NO$_2$ (3) derivative, followed in all cases by an hyperchromic effect in relation to the corresponding ω-ethylthioacetophenones (15), (13) and (16).

It should be pointed out that except for compound (3) the bathochromic shifts of the $n \rightarrow \pi^*$ transition noticed for compounds (1)–(9) in relation to the corresponding acetophenones (10)–(12) are in line with the previously proposed hyperconjugative interaction for the ω-ethylthioacetophenones[1] between the π^*_{CO} and $\sigma^*_{\mathrm{C\text{-}S}}$ orbitals which should also occur for the *gauche* rotamers of the ω-(*p*-phenylthio)-*p*-substituted acetophenones. This interaction leads to a stabilization of the π^*_{CO} orbital in relation to the carbonyl oxygen lone pair $n_{\mathrm{O(CO)}}$ and therefore to a bathochromic shift of the $n \rightarrow \pi^*$ transition (Figure 6).

It should be mentioned that practically the same $n \rightarrow \pi^*_{\mathrm{CO}}$ transition energy is envolved in the acetophenone derivatives (1) and (2), (4) and (5), (7) and (8), containing at the phenacyl group the same *para* substituents and at the *para* position of the phenylthio group the methoxy and hydrogen substituents. This fact is indicative that both π^*_{CO} and $n_{\mathrm{O(CO)}}$ energy levels are destabilized by the same amount on going from hydrogen ($\sigma_p = 0$) to methoxy ($\sigma_p = -0.27$[17]) *para* sub-

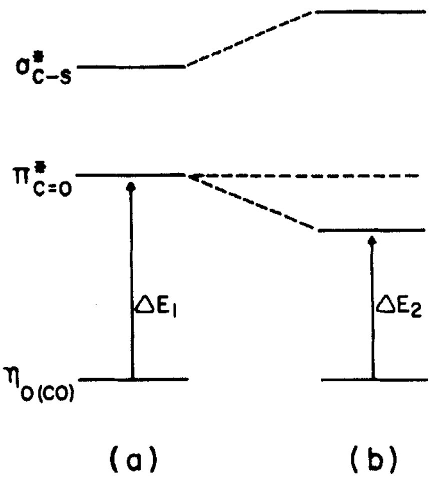


FIGURE 6 Qualitative energy levels of the $\sigma^*_{\mathrm{C\text{-}S}}$ and π^*_{CO} orbitals for the *gauche* rotamers of ω-(*p*-phenylthio)-*p*-substituted acetophenones before (a) and after (b) orbitals interaction.

stituents at the phenylthio group, leading after the hyperconjugative interaction practically to the same $n \rightarrow \pi^*$ energy gap. This explanation is supported by the occurrence of approximately the same $n \rightarrow \pi^*$ transition energies in the corresponding *para*-substituted ω-ethylthioacetophenones (16) and (13) (Table VIII).

On the other hand the progressive smaller bathochromic shift of the $n \rightarrow \pi^*$ transition of the *p*-nitrophenylthio derivatives (9), (6) and the abnormal large hypsochromic shift of compound (3) in relation to the corresponding acetophenones (10)–(12) is in disagreement with what was expected from the above trend i.e. the stabilization of both the π^*_{CO} and $n_{O(CO)}$ levels by practically the same amount on going from hydrogen to the electron-attracting nitro (σ_p = +0.78[17]) substituent at the *para* position of the phenylthio group.

In fact the experimental trend for the *p*-nitrophenylthio derivatives (3), (6) and (9) suggests that the π^*_{CO} orbital is progressively stabilized in a lesser extent than the carbonyl oxygen lone pair, leading after $\pi^*_{CO}/\sigma^*_{C\text{-}S}$ hyperconjugation to progressive higher energy gaps.

Due to the electron-attracting effect of the *p*-nitrophenylthio substituent, it seems reasonable to speculate that the greater stabilization of the $\sigma^*_{C\text{-}S}$ orbital in the *p*-nitrophenylthioacetophenones should play some important role in determining the energy of the π^*_{CO} orbital and therefore in the $n \rightarrow \pi^*_{CO}$ transition. However, we hope that M.O. studies which are in progress may clarify this behavior.

EXPERIMENTAL

Materials. All solvents for spectrometric measurements were spectrograde and were used without further purification. ω-(*p*-phenylthio)-*p*-substituted acetophenones X-ϕC(O)CH$_2$Sϕ-Y, where *X* and *Y* are respectively: H, H (5)[18]; H, OMe (4)[19]; OMe, H (8)[19]; OMe, OMe (7)[20]; NO$_2$, H (2)[21]; H, NO$_2$ (6)[22]; OMe, NO$_2$ (9), MP 124–126° (Lit.[23] = 158°); ^{1}H NMR (CDCl$_3$): δ 3.88 (s, 3H, CH$_3$O); 4.39 (s, 2H, CH$_2$); 6.86 (d, 2H, *J* = 7.5 Hz, Ar); 7.41 (d, 2H, *J* = 7.5 Hz, Ar); 8.09 (d, 2H, *J* = 7.5 Hz, Ar). Anal. Calcd. for $C_{15}H_{13}NO_4S$: C, 59.39; H, 4.32; N, 4.62; S, 11.72. Found: C, 59.34; H, 4.65; N, 4.90; S, 11.76, were obtained following practically the same procedure described for ω-ethyl-thioacetophenones[1] i.e. from an ethanolic solution of ω-bromo-*p*-substituted acetophenone[24] and sodium *p*-substituted thiophenolate at room temperature. The NO$_2$, OMe (1) derivative, MP 65–71° (from ethanol 95%) is a new compound and was prepared by the same procedure; ^{1}H NMR (CDCl$_3$): δ 3.72 (s, 3H, CH$_3$O); 4.05 (s, 2H, CH$_2$); 6.69 (d, 2H, *J* = 8.5 Hz, Ar); 7.20 (d, 2H, *J* = 8.5 Hz, Ar); 7.88 (d, 2H, *J* = 8.7 Hz, Ar); 8.13 (d, 2H, *J* = 8.7 Hz, Ar). Anal. Calcd. for $C_{15}H_{13}NO_4S$: C, 59.39; H, 4.32; N, 4.62; S, 10.57. Found: C, 59.05; H, 4.33; N, 4.74; S, 10.47.

The NO$_2$, NO$_2$ (3) derivative, MP 195–199° (Lit.[23] = 160°); ^{1}H NMR (DMSO-d$_6$): δ 5.61 (s, 2H, CH$_2$); 8.10 (d, 2H, *J* = 2.6 Hz, Ar); 8.67 (d, 2H, *J* = 2.6 Hz, Ar); 8.83 (d, 2H, *J* = 2.6 Hz, Ar); 8.92 (d, 2H, *J* = 2.6 Hz, Ar). Anal. Calcd. for $C_{14}H_{10}N_2O_5S$: C, 52.83; H, 3.17; N, 8.80; S, 10.07. Found: C, 53.18; H, 3.26; N, 8.97; S, 10.14, was prepared essentially by the same procedure described above, using acetone as solvent instead of ethanol. The sodium *p*-nitrophenylthiophenolate[25,26] was prepared in a different way i.e. from an ethanolic solution of *p,p'*-dinitro-diphenyl-disulfide with sodium sulfide and potassium hydroxide.

I.R. Measurements. The conditions for recording the I.R. carbonyl stretching bands in both fundamental (1800–1500 cm^{-1}) and in the first overtone (3500–3200 cm^{-1}) regions for 2×10^{-2} *M* solutions of the title compounds (1)–(9), in *n*-hexane, carbon tetrachloride and chloroform, using 0.2 mm calcium fluoride and 1.00 cm quartz matched cells, respectively, have already been described.[3] For the majority of the studied compounds the higher frequency component of the doublet is a shoulder of the lower frequency component. Taking into account that in general the background is not parallel to the wave-number axis due to a significant overlapping between the lower frequency band of the doublet and the ring stretching bands which occur near 1600 cm^{-1}, the graphical decomposition of the doublet was precluded. Thus, the frequency for the *cis* rotamer was estimated directly at the inflexion point of the overlapped band. The *cis/gauche* relative concentrations were estimated from the ratio of the absorbances of the two overlapped bands, measured directly at the inflexion point and at the absorption maximum, assuming as an approximation the equality of the molar absorption coefficients of the two rotamers. The carbonyl frequencies for the more and less intense components of the doublet are accurate in the fundamental and in the 1st overtone regions to ±0.5 and ±1 cm^{-1} and ±1 and ±2 cm^{-1}, respectively. Due to the large scale expansion employed for compounds (1), (2) and (8), in *n*-hexane, the shoulder corresponding to the *cis* rotamer can be mislaid with the noise therefore precluding the determination of the frequency of the inflexion point of the band.

The U.V. spectra of 10^{-3} – 10^{-2} *M* solutions in *n*-hexane, and ^{13}C NMR spectra of the 0.5 *M* solutions of the title compounds in $CDCl_3$ were obtained as previously[9,27] described. Due to the very low solubility of compound (3) in the majority of the organic solvents employed, the ^1H and ^{13}C NMR spectra of this compound were recorded in dimethyl-d_6 sulfoxide and the I.R. spectrum was recorded only in chloroform.

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