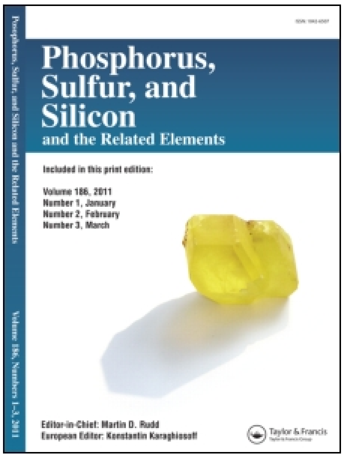

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CONFORMATIONAL AND ELECTRONIC INTERACTION STUDIES OF α-SUBSTITUTED CARBONYL COMPOUNDS. VI. *p*-SUBSTITUTED α-PHENYLTHIOACETONES.

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The analysis of the ν_{CO} bands in the I. R. spectrum of *p*-substituted α-phenylthioacetones indicates a *cis/gauche* rotational isomerism. The slight solvent effect on the α_c/α_g ratios on going from a non polar solvent to a polar one, for the title compounds, as well as the minute sensitivity of the ν_{CO} (*cis*) frequencies on going from electron-attracting to electron-donating substituents are interpreted on the grounds of the Field (F) and Inductive (I) Effects, which act in opposition in the *cis* rotamer, practically cancelling each other. The decreasing *cis/gauche* population ratio on going from electron-attracting to electron-donating substituents suggests the occurrence of the hyperconjugative interaction in the *gauche* rotamers of the title compounds. The progressive shielding effect on the methylene and carbonyl carbon atoms in the ^{13}C NMR spectra, on going from electron-donating to electron-attracting substituents is ascribed at least in part, to the "Reserve Polar Effect".

Key words: Conformational studies; electronic interaction; Reverse Polar Effect; I.R. spectroscopy; ^{13}C NMR spectroscopy; *p*-substituted α-phenylthioacetones.

Previous reports from this laboratory on α-heterosubstituted acetones[1,2] and ω-ethylthio-*p*-substituted acetophenones[3] have suggested the existence of hyperconjugative interaction between π_{CO} and σ_{C-S} orbitals both in the ground and excited states as well as the occurrence of charge transfer from π_{CO} to $3d_{(S)}$ orbitals in the *gauche* rotamers of such compounds.

This paper deals with I.R. and ^{13}C NMR studies of some *p*-substituted α-phenylthioacetones containing electron-attracting, hydrogen and electron-donating substituents. These compounds were chosen considering that the π_{CO}/σ_{C-S} hyperconjugation as well as the $\pi_{CO} \rightarrow 3d_{(S)}$ charge transfer would be directly affected by the variation of the electronic density at the sulfur atom in the arylthio group, on going from electron-donating to electron-accepting substituents. This, in its turn, would affect the spectroscopic properties of the title compounds.

RESULTS AND DISCUSSION

Table I shows the carbonyl stretching frequencies and the absorbance ratios of the higher and lower frequency components for the *p*-substituted-α-

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phenylthioacetones (1)–(6), in CCl_4 and $CHCl_3$, as well as the corresponding data for the *cis* and *gauche* rotamers of the ethylthioacetone (7). The inspection of this Table shows that, on going from a non polar solvent (CCl_4) to a polar one (chloroform), there is a slight increase in the absorbance ratios of the two components (α_c/α_g). This solvent effect decreases progressively on going from electron-attracting to electron-donating *para* substituents, vanishing for the *p*-amino derivative (7). Such a solvent effect is not a definite evidence of the *cis/gauche* rotational isomerism.[4] On the other hand, the fact the differences between the carbonyl stretching frequencies of the *cis* (ν_c) and the *gauche* (ν_g) conformers for the ethylthioacetone (7), in both solvents, are practically the same as those between the higher and the lower frequency components of the carbonyl stretching bands for the *p*-substituted α-phenylthioacetones (1)–(6) (i.e. *ca.* $20\,cm^{-1}$ for carbon tetrachloride and *ca.* $24\,cm^{-1}$ for chloroform), is a strong indication of the *cis/gauche* conformational isomerism,[5] practically ruling out the occurrence of any other vibrational effect. So, it may be assumed that the higher frequency band corresponds to the *cis* (structure I) and the lower frequency band to the *gauche* rotamer (structure II) (Figure 1).

It should also be noticed in Table I that while there is a progressive decrease of the ν_{CO} frequencies of the *gauche* conformers for the phenylthioacetones (1)–(6), in both solvents, on going from electron-accepting to electron-donating *para substituents* ($\nu_{CO} = 6.5\sigma_p^6 + 1706$; $r = 0.990$; *in* $CHCl_3$), in the case of the *cis* conformers there is only a small variation in the ν_{CO} frequencies.

Both the slight solvent effect observed on the α_c/α_g ratios on going from a non polar solvent to a polar one in the *p*-substituted-α-phenylthioacetones and the small sensitivity of the $\nu_{CO\,(cis)}$ frequencies, on going from electron-attracting to electron-donating *para* substituents may be explained analysing the two extremes cases (structure III and IV, Figure 2) of the *cis* conformers for the title compounds, as follows.

If the phenylthioacetones bear in the *para* position a strong electron-attracting substituent, there will be a formal positive charge at the sulfur atom (structure III, Figure 2), originating a strong $-I_\sigma$ inductive effect[7] which transmitted through the bonds to the carbonyl group will lead to an increasing double bond character and a decreasing in the normal polarization of this group. On the other hand, the positive charge at the sulfur atom will induce through space a stronger electrostatic attraction between the positively charged sulfur atom and the carbonyl oxygen atom, having now a smaller negative formal charge (Cooperative Field Effect),[7] leading as a consequence, to a decrease in the carbonyl double bond character, practically cancelling out the ($-I_\sigma$) inductive effect.

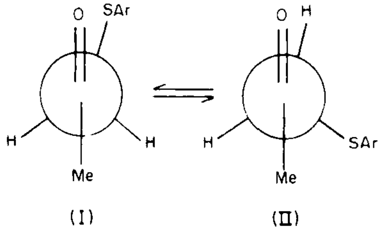


FIGURE 1 *Cis* and *gauche* rotamers of *p*-substituted α-phenylthioacetones.

TABLE I

Frequencies and intensity ratios of the carbonyl stretching bands in the infrared spectra of *p*-substituted-α-phenylthioacetones X—ϕ—$SCH_2C(O)CH_3$ and of ethylthioacetone $CH_2SEtC(O)CH_3$ (7)

		CCl_4		$CHCl_3$	
Comp.	Y	$\nu^{a,b}$	$\alpha_c/\alpha_g{}^c$	ν	α_c/α_g
(1)	NO_2	1733		1732	
		1716	0.27	1711	0.37
(2)	Cl	1733		1730	
		1715	0.24	1708	0.30
(3)	H	1734		1731	
		1714	0.20	1707	0.24
(4)	Me	1733		1730	
		1713	0.19	1705	0.22
(5)	OMe	1731		1728	
		1712	0.18	1704	0.21
(6)	NH_2	1730		1727	
		1710	0.14	1702	0.14
(7)	—[d]	1730		1725	
		1709	0.9	1701	0.23

[a] In cm^{-1}.

[b] The higher and the lower frequencies were determined respectively at the inflexion point and at the maximum of the two overlapping carbonyl stretching bands.

[c] Ratio of the absorbances of the *cis* (c) and *gauche* (g) rotamers respectively.

[d] Data taken from Reference (1).

In the opposite case, if the title compounds bear in *para* position a strong electron-donating substituent, there will be a formal negative charge at the sulfur atom (structure IV, Figure 2) originating a strong $+I_\sigma$ inductive effect[7] leading to a decrease in the carbonyl double bond character and consequently to an increase in the negative formal charge at the carbonyl oxygen atom. The repulsion between the negatively charged sulfur and oxygen atoms leads to a stronger repulsive Field Effect[7] and as a consequence to an increase in the double bond character almost cancelling out the $+I_\sigma$ inductive effect. So, the practically invariation of the carbonyl double bond character in the two extremes cases analyzed should be responsible for the small change in the carbonyl force

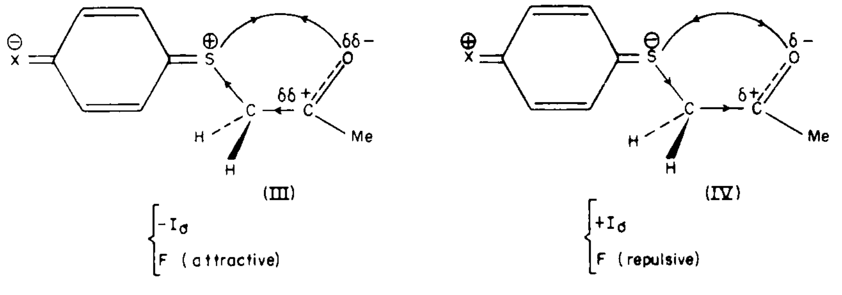
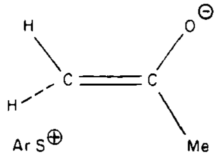


FIGURE 2 *Cis* conformers for *p*-substituted α-phenylthioacetones showing the Field (F) and the Inductive (I) Effects acting in opposition in both structures.



(V)

FIGURE 3 Hyperconjugative structure for the *gauche* rotamers of the *p*-substituted-α-phenylthioacetones.

constants and consequently in the ν_{CO} frequencies as well as in the slight polarity variation of the carbonyl group for the *cis* rotamers in the whole series of the *p*-substituted-α-phenylthioacetones, in both solvents.

The progressive decrease in the *cis*/*gauche* relative population, in both solvents, on going from electron-attracting to electron-donating *para* substituents, in the α-phenylthioacetones series (1)–(6) (Table I) ($\alpha_c/\alpha_g = 0.61\sigma_p + 0.25$; $r = 0.992$; in $CHCl_3$), may be ascribed to the increasing stabilization of the *gauche* conformers. This trend is in good agreement with the previously proposed ($\pi_{CO}/\sigma_{C\text{-}S}$ and π^*_{CO}/n_S) hyperconjugative interaction in the *gauche* conformers of the 2-thiasubstituted carbonyl compounds.[3,8] In fact, it should be pointed out that in the Valence Bond theory, there is an increasing contribution of the dipolar structure V (Figure 3), on going from electron-attracting to electron-donating *para* substituents of the title compounds, leading as a consequence to a progressive stabilization of the *gauche* conformers.

Table II shows the ^{13}C NMR data for the methylene, methyl and carbonyl carbons of the *p*-substituted-α-phenylthioacetones (1)–(6), in $CDCl_3$. Table III shows the ^{13}C NMR data for the methylene and cyano carbons of the *p*-substituted-α-phenylthioacetonitriles (8)–(14) and Table IV presents the ^{13}C NMR data for methylene and methyl carbons of the *p*-substituted phenylethylsulfides (15)–(20), in $CDCl_3$. The latter Tables were included for comparison purposes.

Inspection of Table II shows that while there is only a slight progressive shielding effect for both the carbonyl carbon (1.57 ppm) and methyl carbon (0.22 ppm) on going from electron-donating (NH_2) to electron-accepting (NO_2) *para* substituents of the title compounds, in the case of the methylene carbon

TABLE II

^{13}C NMR chemical shifts[a] for methylene, methyl and carbonyl groups of *p*-substituted-α-phenylthioacetones $X{-}\phi{-}SCH_2C(O)CH_3$, in $CDCl_3$.

X	Comp.	δ_{CO}	δ_{CH_2}	δ_{CH_3}
NO_2	(1)	201.64	42.58	27.68
Cl	(2)	203.08	44.44	27.71
H	(3)	203.16	44.48	27.75
Me	(4)	203.23	45.15	27.74
OMe	(5)	203.23	46.32	27.82
NH_2	(6)	203.31	46.93	27.90

[a] In ppm relative to TMS.

TABLE III

^{13}C NMR chemical shifts[a] for methylene and cyano groups of p-substituted-α-phenylthioacetonitriles $X—\phi—SCH_2C{\equiv}N$, in $CDCl_3$.

X	Comp.	δ_{CN}	δ_{CH_2}
NO_2	(8)	115.22	18.91
Cl	(9)	116.02	21.36
H	(10)	116.29	21.01
Me	(11)	116.44	21.73
CMe_3	(12)	116.51	21.53
OMe	(13)	116.51	22.64
NH_2	(14)	116.82	23.06

[a] In ppm relative to TMS.

a stronger shielding effect is observed (4.35 ppm) ($\delta_{CH_2} = -3.04\sigma_p + 44.93$; $r = 0.992$).

It is worth noting that practically the same shielding effect has been observed in the case of the cyano and the methylene carbons for the p-substituted-α-phenylthioacetonitriles ($\Delta\delta_{CN} = 1.60$ ppm and $\Delta\delta_{CH_2} = 4.15$ ppm, between the NH_2 (14) and NO_2 (8) derivatives (Table III), as well as for the methyl and methylene carbons for the p-substituted phenylethylsulfides ($\Delta\delta_{CH_3} = 0.92$ ppm and $\Delta\delta_{CH_2} = 4.09$ ppm, between NH_2 (20) and NO_2 (15) derivatives (Table IV), on going from electron-donating to electron-accepting *para* substituents.

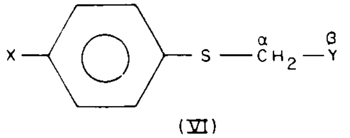
TABLE IV

^{13}C NMR chemical shifts[a] for methylene and methyl groups of some p-substituted ethylphenylsulfides $X—\phi—SCH_2CH_3$, in $CDCl_3$.

X	Comp.	δ_{CH_2}	δ_{CH_3}
NO_2	(15)	25.99	13.53
Cl	(16)	27.87	14.13
H	(17)	27.48	14.17
Me	(18)	28.24	14.33
OMe	(19)	29.60	14.43
NH_2	(20)	30.08	14.45

[a] In ppm relative to TMS.

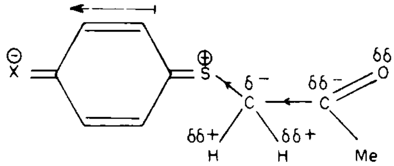
The greater shielding effect on the α carbon atom (methylene group) in relation to the β carbon atom ($C{=}O$, $C{\equiv}N$ and CH_3 groups), which is observed in the three series of compounds (structure VI, Figure 4), on going from



(VI)

Y: $C{=}O$, $C{\equiv}N$ and CH_3

FIGURE 4 General structure for the p-substituted α-phenylthioacetones, α-phenylthioacetonitriles and α-phenylethylthioethers.



(VII)

FIGURE 5 Structure of a α-phenylthioacetone bearing at the *para* position a strong electron-attracting substituent inducing a through bond and through space polarization on the methylene and carbonyl groups.

electron-donating to electron-attracting *para* substituents, may be at least in part ascribed to the occurrence of the 'Reverse Polar Effect".[9,10]

In fact, considering the α-phenylthioacetone having a strong electron-attracting *para* substituent (structure VII, Figure 5), the arylthio dipole will induce through bonds as well as through space (Reserve Polar Effect) a strong polarization on the electronic cloud of the pseudo π_{CH_2} orbital[11,12] and only in a lesser extent, on the electronic cloud of the π_{CO} orbital which is in β position. Consequently the α carbon atoms in the three series of studied compounds should present a greater shielding effect than the β carbon atoms, in the ^{13}C NMR spectra.

It should also be pointed out that the progressive deshielding effect observed on the methylene protons on going from electron-donating to electron-attracting *para* substituents (Table V) ($\delta_{CH_2} = 0.25\sigma_p + 3.62$; $r = 0.981$) goes in opposite direction in relation to the progressive shielding on the methylene carbons of the *p*-substituted α-phenylthioacetones (Table II). So, this trend strongly supports the proposed reversed polarization on the methylene group in structure (VII) (Figure 5).

TABLE V

^{1}H NMR chemical shifts[a] for the methylene protons of *p*-substituted α-phenylthioacetones X—ϕ—SCH$_2$C(O)CH$_3$, in CDCl$_3$.

X	Comp.	δ_{CH_2}
NO$_2$	(1)	3.82
Cl	(2)	3.65
H	(3)	3.66
Me	(4)	3.60
OMe	(5)	3.54
NH$_2$	(6)	3.45

[a] In ppm relative to TMS.

EXPERIMENTAL

Materials. All solvents for spectrometric measurements were spectrograde and were used without further purification.

p-Nitro[13] (1), *p*-chloro[14] (2), *p*-methyl[15] (4) and *p*-methoxy[15] (5) α-phenylthioacetones were obtained following the same procedure described for α-phenylthioacetone[16] i.e. from an aqueous sodium hydroxide solution of the *p*-substituted thiophenol and chloroacetone at 20°C. *p*-Amino-α-phenylthioacetone (6) is a new compound and was prepared by the same procedure. The crude *p*-amino derivative (6) is a yellowish viscous liquid which decomposes when submitted to normal vacuum distillation (>10^{-1} Torr) but it was obtained in pure form by molecular distallation at *ca.* 10^{-4} Torr and at a bath temperature of 100°C: ^{1}H RMN($CDCl_3$); δ 2.23 (s, 3H, $\underline{CH_3}$), 3.45 (s, 2H, $\underline{CH_2}$), 3.59 (s, 2H, $\underline{NH_2}$), 6.58 (d, 2H, J = 8.5 Hz, $\underline{Ar}$), 7.22 (d, 2H, J = 8.5 Hz, $\underline{Ar}$). Anal. Calcd. for $C_9H_{11}NOS$: C, 59.66; H, 6.07; N, 7.73; S, 17.68. Found: C, 60.00; H, 6.19; N, 7.77; S, 17.86.

p-Nitro[17] (15), *p*-chloro[18] (16), *p*-hydrogen[19] (17), *p*-methyl[20] (18), *p*-amino[21] (20) phenylethylsulfides were obtained following, the method described for the *p*-methoxyphenylethylsulfide[22] (19), i.e. from an ethanolic solution of sodium *p*-substituted thiophenolate and ethyl iodide at reflux temperature.

The preparation of the *p*-substituted-α-phenylthioacetonitriles (8)–(19) have already been described.[23]

I.R. and NMR measurements. The conditions for recording the I.R., ^{13}C and ^{1}H NMR spectra have been described elsewhere.[3]

The *cis/gauche* relative concentrations were estimated in the I.R. spectra from the ratio of the two superimposed carbonyl bands, assuming as an approximation the equality of the molar absorptivities of the two rotamers. The frequency for the *cis* rotamer was estimated directly at the inflexion point of the overlapped band.

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