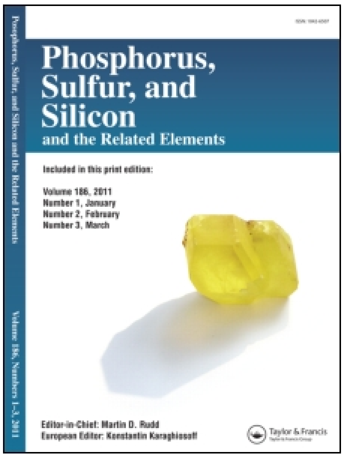

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CONFORMATIONAL STUDIES OF α-SUBSTITUTED CARBONYL COMPOUNDS. IV. ELECTRONIC INTERACTION IN 2-THIASUBSTITUTED CARBONYL SYSTEMS. ω-ETHYLTHIO-*p*-SUBSTITUTED ACETOPHENONES

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CONFORMATIONAL STUDIES OF α-SUBSTITUTED CARBONYL COMPOUNDS. IV. ELECTRONIC INTERACTION IN 2-THIASUBSTITUTED CARBONYL SYSTEMS. ω-ETHYLTHIO-*p*-SUBSTITUTED ACETOPHENONES[1]

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The carbonyl stretching frequencies and the apparent molar absorptivities are reported for some ω-ethylthio-*p*-substituted acetophenones and for the corresponding unsubstituted acetophenones. In the ω-ethylthio- series the solvent effect indicates the presence of the *cis*/*gauche* rotational isomerism, being the *gauche* rotamer predominant in the whole series (ca. 90%). In the ω-ethylthioacetophenones, on going from electron-attracting to electron-donating substituents, the progressive increase in the carbonyl *cis* shifts ($\Delta\nu_c$) is attributed to the increasing Field Effect between C═O and C—S dipoles, and the progressive decrease in the carbonyl *gauche* shifts ($\Delta\nu_g$) is due to the deacreasing contribution of the hyperconjugative interaction between π_{CO} and σ_{C-S} orbitals. The U.V. spectra of the ω-ethylthioacetophenones display a $n \rightarrow \pi^*_{CO}$ band which is bathochromically shifted in relation to the corresponding acetophenones, indicating the occurrence of the hyperconjugative interaction between π^*_{CO} and σ^*_{C-S} orbitals in the excited state. ^{13}C NMR data for the methylene group of ω-ethylthioacetophenones, compared to those for some ω-haloacetophenones,[2,3] suggest that in the fundamental state besides the hyperconjugative interaction, there is also the occurrence of charge transfer from π_{CO} to $3d_{(S)}$ orbitals.

Previous reports from this laboratory[4] on the α-hetero-substituted acetones have shown that the low energy σ_{C-S} bond makes the hyperconjugative interaction with π_{CO} orbital easier, both in the ground and in the excited state, for the *gauche* rotamers of some α-alkylthioacetones. Similarly, the hyperconjugative interaction was reported for the α-thiosubstituted cyclanones.[5]

This paper deals with I.R., ^{13}C NMR and U.V. studies of some ω-ethylthio-*p*-substituted acetophenones containing electron-attracting, hydrogen and electron-donating substituents. These compounds were chosen for the following reasons: the steric effect of the substituent directly linked to the carbonyl group (always an

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aryl group) is constant; considering the possibility of hyperconjugation between π_{CO} and σ_{C-S} and between the corresponding antibonding orbitals, in the *gauche* rotamers, such interactions would be directly affected by varying the conjugation in the phenacyl group on going from electron-attracting to electron-donating substituents. This would affect the spectroscopic properties of such model compounds.

RESULTS AND DISCUSSION

Table I shows the carbonyl stretching frequencies, the corresponding apparent molar absorptivities and the ratios between the molar absorptivities of the higher and lower frequency components for the ω-ethylthio-*p*-substituted acetophenones (**1**)–(**8**), in *n*-hexane and chloroform. The inspection of this Table shows that, on going from a non polar solvent (*n*-hexane) to a polar one (chloroform), the ratio between the molar absorptivities of the two components ($\varepsilon_c/\varepsilon_g$) is approximately twice bigger in the polar solvent. This solvent effect suggests a *cis/gauche* conformational equilibrium[6a] and practically excludes the Fermi Resonance. It may be assumed that the higher frequency band corresponds to the *cis* (C) and the lower frequency band to the *gauche* rotamer (G) (Figure 1).

TABLE I

Frequencies and intensities of the carbonyl stretching bands in the infrared spectra of ω-ethylthio-*p*-substituted acetophenones Y-ϕ-C(O)CH$_2$SEt

		n-C_6H_{14}			$CHCl_3$		
Comp.	Y	ν[a]	ε[b]	$\varepsilon_c/\varepsilon_g$[c]	ν	ε	$\varepsilon_c/\varepsilon_g$
(**1**)	NO_2	1703	36		1698	56	
		1687.6	438	0.08	1682.6	402	0.14
(**2**)	CN	1703	28		1700	69	
		1685.9	380	0.07	1679.6	353	0.19
(**3**)	Br	1700	30		1696	78	
		1681.4	460	0.06	1674.6	392	0.20
(**4**)	Cl	1702	31		1691	58	
		1682.1	439	0.07	1673.4	324	0.16
(**5**)	H	1700	41		1692	50	
		1680.8	469	0.09	1673.4	293	0.17
(**6**)	Me	1697	30		1688	49	
		1678.5	524	0.06	1669.9	382	0.13
(**7**)	OMe[d]	1690			1686		
		1675.0	545	—	1665.5	364	—
(**8**)	NH_2	—[e]			1676[d]		
		1669.6		—	1657.8	332	—

[a] In cm^{-1}.

[b] Apparent molar absorptivity in l mol^{-1} cm^{-1}.

[c] Subscripts *c* and *g* indicate *cis* and *gauche* rotamers respectively.

[d] The frequency for the *cis* rotamers was estimated directly at the inflexion point of the band.

[e] See Experimental part.

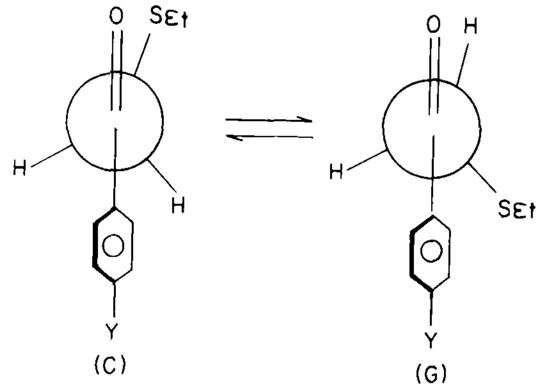

FIGURE 1 *cis* and *gauche* rotamers of ψ-ethylthio-p-substituted acetophenones.

Table I also shows that the *cis*/*gauche* ratio for the ω-ethylthio-p-substituted acetophenones, on going from electron-attracting to electron-donating substituents (**1**)–(**8**), is practically constant in both solvents, being the *gauche* rotamer predominant (ca. 90%).

With the aim of studying the carbonyl stretching frequencies shifts ($\Delta\nu$) for this *cis* and *gauche* rotamers of the ω-ethylthio-p-substituted acetophenones, in relation to the corresponding p-substituted acetophenones, the carbonyl stretching frequencies of the latter compounds (**9**)–(**16**) were measured in n-hexane and chloroform (Table II).

Table III shows the frequency shifts for the *cis* and *gauche* rotamers, $\Delta\nu_C$ and $\Delta\nu_g$, respectively. It can be noticed that the carbonyl frequency shifts for the *cis* rotamers are always positive whilst those for the *gauche* rotamers are always negative. These results also show that, for both solvents, there is a progressive increase for the *cis* shifts on going from electron-attracting to electron-donating substituents and that the absolute values for the *gauche* shifts are progressively smaller on going from electron-attracting to electron-donating substituents. The

TABLE II

Carbonyl stretching frequencies[a] of p-substituted acetophenones Y-ϕ-C(O)CH$_3$

Compd.	*Y*	n-C_6H_{14}	$CHCl_3$
(**9**)	NO_2	1703.1	1693.5
(**10**)	CN	1700.9	1691.7
(**11**)	Br	1695.7	1684.6
(**12**)	Cl	1696.1	1683.4
(**13**)	H	1694.6	1682.8
(**14**)	Me	1691.5	1676.8
(**15**)	OMe	1686.9	1673.0
(**16**)	NH_2	1681.7	1664.0

[a] In cm^{-1}.

TABLE III

Carbonyl frequency shifts[a] for the *cis* ($\Delta\nu_c$) and *gauche* ($\Delta\nu_g$) rotamers of ω-ethylthio-p-substituted acetophenones

		n-C_6H_{14}		$CHCl_3$	
Compds.	Subst.	$\Delta\nu_c$	$\Delta\nu_g$	$\Delta\nu_c$	$\Delta\nu_g$
(1)–**(9)**	NO_2	0	−15.5	4	−10.9
(2)–**(10)**	CN	2	−15.0	8	−12.1
(3)–**(11)**	Br	4	−14.3	11	−10.0
(4)–**(12)**	Cl	4	−14.0	8	−10.0
(5)–**(13)**	H	5	−13.8	9	−9.4
(6)–**(14)**	Me	5	−13.0	11	−6.9
(7)–**(15)**	OMe	—	−11.9	—	−7.5
(8)–**(16)**	NH_2	—	−12.1	—	−6.2

[a] $\Delta\nu_c$ and $\Delta\nu_g$ in cm^{-1}, refers to the difference: ν(ω-ethylthio-p-substituted acetophenone) − ν(parent acetophenone).

progressive increase of the *cis* shifts ($\Delta\nu_C$) may be attributed to the progressive contribution of the more polar carbonyl structure (Figure 2, structure II). This will cause an increase in the Field Effect[6b] originated from a stronger repulsion between the C=O and C—S dipoles. As a consequence the carbonyl frequencies as well as the *cis* shifts will be larger.

The decrease of the *gauche* shifts on going from electron-attracting to electron-donating substituents may be explained by the following considerations.

As reported previously for the α-hetero-substituted acetones,[4] the progressive decrease in the carbonyl frequencies and, consequently, in the carbonyl force constants is due to an increasing contribution of the hyperconjugative interaction

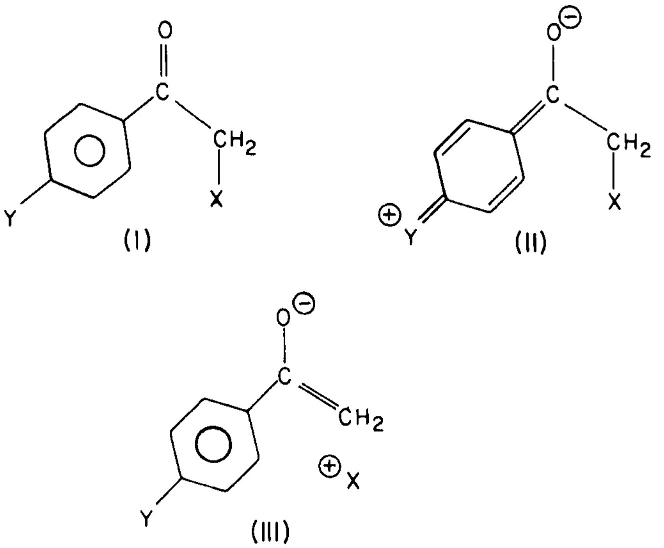

FIGURE 2 Resonance structures for the ω-hetero-p-substituted acetophenones.

between $\pi_{CO} - \sigma_{C-X}$ orbitals. It seems reasonable to admit, in the V.B. theory, that besides the Resonance Structures (I) and (II) (Figure 2), present in the *p*-substituted acetophenones, there will be also the contribution of the hyperconjugative structure (III), for the ω-ethylthioacetophenones. This contribution will increase as the conjugation between the *para* substituent and the carbonyl group, in the phenacyl system decreases. In fact, the carbonyl frequency shifts presented in Table III are in line with these predictions.

The small carbonyl frequency shift observed for the *p*-amino compound (**8**) is a consequence of the decrease in the carbonyl force constant, due to a smaller contribution of the hyperconjugative structure. On the other hand, the large frequency shift in the *p*-nitro compound (**1**) results from the decrease in the carbonyl force constant, due to a greater contribution of the hyperconjugative structure.

This kind of analysis according to the V.B. Theory is in agreement with orbital interactions based on the Molecular Orbital Simple Perturbation Theory.[7] Considering a πMO (energy $= E_\pi$) and σMO (Energy $= E_\sigma$), with $E_\sigma < E_\pi$ and providing that the two MOs overlap, the πMO will be destabilized by $|\delta E|$ and the σMO stabilized by $|\delta E|$, being $|\delta E|$ given by the equation:

$$\delta E = \frac{(H_{\sigma\pi})^2}{\Delta E}$$

where $\Delta E = |E_\pi - E_\sigma|$, and $H_{\sigma\pi}$ is a measure of the interaction between the σ and πMOs.

For the *p*-substituted acetophenones, containing electron-attracting substituents, the double bond character of the carbonyl group will be larger and, therefore, the π_{CO} orbital will have a higher ionization potential. On the contrary, lower ionization potentials, will be expected for acetophenones containing electron-donating substituents.

As an approximation the π_{CO} orbital of some aliphatic ketones (I.P. ca. 12 ev)[8] and the σ_{C-S} orbital of the ethanethiol (I.P. 13.7 ev)[9] (Figure 3) can be considered as being unperturbed orbitals for the ω-ethylthio-*p*-substituted

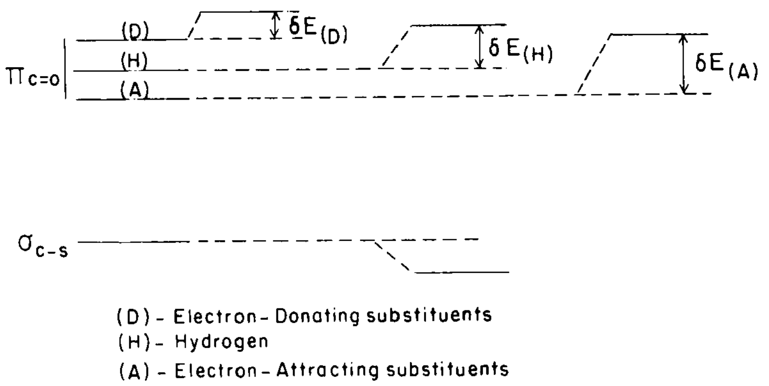

FIGURE 3 Qualitative energy levels diagram for the σ_{C-S} and π_{C-O} orbitals for the *gauche* rotamers of ω-ethylthio-*p*-substituted acetophenones before and after orbitals interaction.

TABLE IV

U.V. data for the carbonyl $n \rightarrow \pi^*$ transition of the acetophenones Y-ϕ-C(O)CH$_2$X, in *n*-hexane

	$X = H$			$X = SEt$		
Y	Comp.	$\lambda^{a,b}$	ε^{c}	Comp.	λ^{a}	ε^{c}
OMe	**(15)**	315	95	**(7)**	332	890
Me	**(14)**	316	56	**(6)**	335	565
H	**(13)**	323	43	**(5)**	339	471
Cl	**(12)**	321	57	**(4)**	339	571
Br	**(11)**	321	64	**(3)**	340	609
CN	**(10)**	325	66	**(2)**	352	862
NO$_2$	**(9)**	325	288	**(1)**	357	766

[a] λ in nm.
[b] Inflexion.
[c] Apparent molar absorptivity in 1 mol^{-1} cm^{-1}.

acetophenones. Assuming that ($H_{\sigma\pi}$) is a constant in the whole acetophenones series it can be easily concluded from this Figure that in the ω-ethylthioacetophenones, containing electron-attracting substituents, the π_{CO} destabilization $|\delta E|$ is greater than in those containing electron-donating substituents, where energy levels of the interacting orbitals are further apart. Therefore, in the ground state there will be a greater hyperconjugative interaction between π_{CO} and σ_{C-S} orbitals in compounds containing electron-attracting substituents than in those containing electron-donating substituents.

Table IV shows the wavelengths and the molar absorptivities, measured on the inflexion points and at the maxima of the $n \rightarrow \pi^*$ carbonyl bands for the acetophenones **(15)**–**(9)** and for the corresponding ω-ethylthioacetophenones **(7)**–**(1)**, in *n*-hexane. The inspection of this Table shows that the introduction of an ethylthio-group in the ω-position of *p*-substituted acetophenones results in a bathochromic shift of the $n \rightarrow \pi^*$ transition band of ca. 20 nm and an intensification of ca. 10 fold.

The bathochromic shift of the $n \rightarrow \pi^*$ band may be explained as follows. Taking into account that the bonding character of the π_{CO} orbital is smaller than that of the σ_{C-S} orbital, the π^*_{CO} orbital should have an antibonding character smaller than that of the σ^*_{C-S} orbital.[10] The interaction of these latter orbitals (Figure 4) should result in a stabilization of the π^*_{CO} orbital by $|\delta E^*|$ and, therefore, leading to a bathochromic shift of the $n \rightarrow \pi^*_{CO}$ transition.

Therefore, it can be concluded that the hyperconjugative interaction should play an important role in the excited state of these compounds, being this behavior in a good agreement with our previous U.V. studies on some ketones,[4,5] containing alkylthio-groups in α-position.

Table IV also shows that there is a bathochromic shift for both series of compounds on going from electron-donating to electron-attracting substituents. These results are in line with those of the ionization potentials and polarographic measurements for the *p*-substituted acetophenones reported in the literature. It was observed[11] that, on going from electron-donating to electron-attracting substituents, there is a progressive increase of the I.P. of the carbonyl oxygen

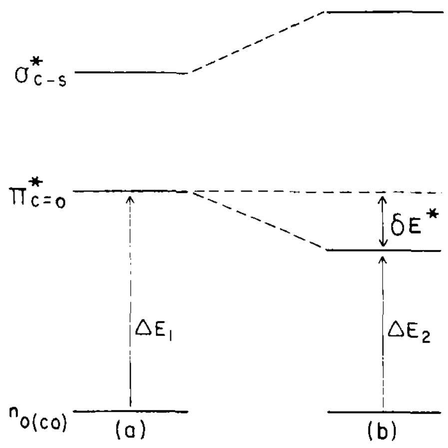

FIGURE 4 Qualitative energy levels for the σ^*_{C-S} and $\pi^*_{C=O}$ orbitals for the *gauche* rotamers of ω-ethylthio-*p*-substituted acetophenones before (a) and after (b) orbitals interaction.

lone pair $n_{O(CO)}$ as well as a simultaneous decrease in the polarographic half-wave reduction potential, being the latter correlated linearly with the LUMO energies. In order to explain the observed bathochromic shifts of the $n \rightarrow \pi^*_{CO}$ transition in the two series of the acetophenones (**15**)–(**9**) and (**7**)–(**1**) it should be assumed a greater stabilization of the LUMO than that of the oxygen lone pair $n_{O(CO)}$, on going from electron-donating to electron-attracting substituents.

However, the inspection of Table IV shows that while in the acetophenone series (**15**)–(**9**) there is a shift of ca. 10 nm, in the ω-ethylthioacetophenone series (**7**)–(**1**) a shift of 25 nm is observed. We cannot offer any explanation for this difference at the moment. However we hope that the He^I photoelectron spectroscopy and ab-initio studies which are in progress may clarify this difference.

In order to confirm the existence of the π_{CO}/σ_{C-S} hyperconjugative interaction in the fundamental state ^{13}C NMR studies of ω-ethylthio-*p*-substituted acetophenones were undertaken and were compared to those on ω-bromo-[2] and ω-iodo-*p*-substituted acetophenones.[3] It should be pointed out that the *gauche* rotamer population is predominant in these three series, being of ca. 90% for the ethylthio- and iodoacetophenone derivatives and of ca. 80% for the bromoacetophenone derivatives.

Table V shows the ^{13}C NMR data for the methylene carbon (in —$COCH_2$— group), for the carbonyl carbon of the ω-ethylthio-*p*-substituted acetophenones (**1**)–(**8**), and for the methyl carbon, as well as for the carbonyl carbon of the *p*-substituted acetophenones (**9**)–(**16**).

It is well known,[12] that the variation on conjugation in the carbonyl group in *p*-substituted acetophenones does not affect significantly the shielding effect on the carbonyl carbon. In fact, it can be noticed in Table V a practically constant carbonyl carbon chemical shifts for both series of acetophenones (**1**)–(**8**) and (**9**)–(**16**), on going from electron-attracting to electron-donating substituents. This

TABLE V

^{13}C NMR chemical shifts[a] for the methylene (in—CH_2CO—), methyl and carbonyl groups of the acetophenones Y-ϕ-C(O)CH_2X, in $CDCl_3$

	$X = SEt$			$X = H$		
Y	Comp.	δ_{CO}	δ_{CH_2}	Comp.	δ_{CO}	δ_{CH_3}
NO_2	**(1)**	192.37	36.77	**(9)**	196.08	26.78
CN	**(2)**	192.57	36.55	**(10)**	196.27	26.53
Br	**(3)**	193.21	36.54	**(11)**	196.77	26.29
Cl	**(4)**	193.06	36.57	**(12)**	196.57	26.35
H	**(5)**	194.32	36.63	**(13)**	197.92	26.41
Me	**(6)**	194.14	36.61	**(14)**	197.60	26.29
OMe	**(7)**	193.22	36.48	**(15)**	196.51	26.11
NH_2	**(8)**	193.09	36.42	**(16)**	196.16	25.69

[a] In ppm relative to TMS.

table also shows a slight, but practically constant upfield shift of ca. 3 ppm for the carbonyl carbon, on going from acetophenones **(9)**–**(16)** to ω-ethylthioacetophenones **(1)**–**(8)**, which may be attributed mainly to the inductive effect of the α-ethylthio group ($\sigma^* = 0.56$).[13]

It can be also observed a slight deshielding effect, both on the methyl carbon of the acetophenones (−0.97 ppm) and on the methylene carbon (in —$COCH_2$—) of the ω-ethylthioacetophenones (−0.35 ppm), on going from electron-donating (NH_2) to electron-attracting (NO_2) substituents. However, it is noteworthy that on the contrary, in the case of ω-bromo-[2] and ω-iodoacetophenones[3] (Table VI),

TABLE VI

^{13}C NMR chemical shifts[a] for the methylene groups of the ω-bromo and ω-iodoacetophenones Y-ϕ-C(O)CH_2X, in $CDCl_3$

	$X = Br$[b]	$X = I$[c]
Y	δ_{CH_2}	
NO_2	29.96	0.77
CN	29.86	0.66
Br	30.19	0.98
Cl	30.17	0.96
H	30.73	1.51
Me	30.68	1.61
OMe	30.46	1.49
NMe_2	30.57	1.89

[a] In ppm relative to TMS.

[b,c] data from References (2) and (3), respectively.

a shielding effect on the methylene carbon was observed, on going from electron-donating to electron-attracting substituents. The deshielding effect on the methylene carbon of the ω-ethylthioacetophenone series seems to indicate that there is not an increase in the double bond character between the methylene carbon and the carbonyl carbon, which according to Nesmeyanov predictions[14] would be indicative of hyperconjugative interaction. In fact, in the case of ω-bromo and ω-iodoacetophenones (Table VI) a shielding effect on the methylene carbon on going from electron-donating (NMe_2) to electron-attracting (NO_2) substituents was observed, being these values of +0.61 and +1.12 ppm, respectively.

Additionally, the experimental shifts for the α-methylene carbon of the ω-ethylthioacetophenones (**1**)–(**8**) are upfield shifted in relation to the calculated[15] values by ca. 8 ppm [e.g. for *ω-ethylthioacetophenone* (**5**), $\delta_{(\text{calc.})} = -2.3 + 28.7 + 18.6 = 45.0$ ppm; $\delta_{(\text{exp.})} = 36.33$ ppm]. However, it should be pointed out that these upfield shifts are smaller than those ones for ω-bromo and ω-iodoacetophenones, for which the values are of ca. 15 ppm [e.g. for *ω-bromoacetophenone,* $\delta_{(\text{calc.})} = -2.3 + 28.7 + 20.0 = 46.4$ ppm; $\delta_{(\text{exp.})} = 30.73$ ppm and for *ω-iodoacetophenone,* $\delta_{(\text{calc.})} = -2.3 + 28.7 - 10.5 = 15.9$ ppm; $\delta_{(\text{exp.})} = 1.51$ ppm]. This behavior also suggests the decreasing contribution of the hyperconjugative structure for the *gauche* rotamer of the ω-ethylthioacetophenones, in comparison to the ω-bromo and ω-iodoacetophenones.

A plausible explanation for this anomalous behavior is that, in addition to the hyperconjugative effect (π_{CO}/σ_{C-S}), there should be another effect. This could be a through-space charge transfer from the π_{CO} to a 3d sulfur orbitals. It is noteworthy that the occurrence of this effect is also in accordance with the I.R. carbonyl shifts. In fact, the increase of the double bond character of the π_{CO} bond (on going from electron-donating to electron-attracting substituents) lead to a greater electron density of the carbonyl π orbital, resulting in an increase of charge transfer to sulfur 3d orbitals. This would cause a progressive decrease in the carbonyl force constant and, therefore, an increase in the frequency shifts (Table III).

EXPERIMENTAL

Materials

All solvents for spectrometric measurements were spectroscopic grade and were used without further purification. Commercial acetophenones (**9**)–(**16**) were purified as described elsewhere.[16]

ω-Ethylthioacetophenone (**5**),[17] ω-ethylthio-*p*-methylacetophenone (**6**),[17]and ω-ethylthio-*p*-methoxyacetophenone (**7**)[17] were obtained from the corresponding ω-bromoacetophenones[18] and sodium ethylmercaptide at 0°C. The following ω-ethylthioacetophenones were prepared by the same method:

ω-Ethylthio-p-nitroacetophenone (**1**), bp 145° (0.30 mm); ^{1}H NMR ($CDCl_3$): δ 1.26 (t, 3H, $J = 5.9$ Hz, CH_3), 2.56 (q, 2H, $J = 5.9$ Hz, $\underline{CH_2}$), 8.06 (d, 2H, $J = 7.1$ Hz, $\underline{\mathrm{Ar}}$), 8.28 (d, 2H, $J = 7.1$ Hz, $\underline{\mathrm{Ar}}$) Anal. calcd. for $C_{10}H_{11}NO_3S$: C, 53.33; H, 4.88; S, 14.22. Found C, 53.47; H, 4.60; S, 14.00.

ω-Ethylthio-p-cyanoacetophenone (**2**), bp 153.0–155.0° (0.60 mm); ^{1}H NMR (CCl_4): δ 1.26 (t, 3H, $J = 5.9$ Hz, $\underline{CH_2}$), 2.49 (q, 2H, $J = 5.9$ Hz, $\underline{CH_2}$), 3.63 (s, 2H, $\underline{CH_2}$), 7.64 (d, 2H, $J = 7.1$ Hz, $\underline{\mathrm{Ar}}$), 7.93 (d, 2H, $J = 7.1$ Hz, $\underline{\mathrm{Ar}}$). Anal. calcd. for $C_{11}H_{10}NOS$: C, 64.39; H, 5.36; S, 15.61. Found: C, 64.29; H, 5.50; S, 15.42.

ω-Ethylthio-p-bromoacetophenone (**3**), bp 140.0–142.0° (0.50 mm); ^{1}H NMR (CCl_4): δ 1.25 (t, 3H, $J = 5.9$ Hz, CH_3), 2.53 (q, 2H, $J = 5.9$ Hz, CH_2); 3.54 (s, 2H, CH_2), 7.40 (d, 2H, $J = 6.9$ Hz, Ar), 7.68 (d, 2H, $J = 6.9$ Hz, Ar). Anal. calcd. for $C_{10}H_{11}BrOS$: C, 46.35; H, 4.25; S, 12.36. Found: C, 46.63; H, 3.93; S, 12.15.

ω-Ethylthio-p-chloroacetophenone (**4**), bp 164.0–165.0° (0.07 mm); ^{1}H NMR (CCl_4): δ 1.24 (t, 3H, $J = 5.9$ Hz, CH_3), 2.51 (q, 2H, $J = 5.9$ Hz, CH_2), 3.60 (s, 2H, CH_2), 7.31 (d, 2H, $J = 6.9$ Hz, Ar), 7.68 (d, 2H, $J = 6.9$ Hz, Ar). Anal. calcd. for $C_{10}H_{11}ClOS$: C, 55.84; H, 5.13; S, 14.92. Found: C, 56.06; H, 5.00; S, 14.90.

ω-Ethylthio-p-aminoacetophenone (**8**), was obtained from the ω-bromo-*p*-(N-acetylamino)acetophenone[19] and sodium ethylmercaptide at 0°C, followed by hydrolises of the crude ω-ethylthio-*p*-(N-acetylamino) acetophenone,[20] MP 68.5–70.5° (from ethanol); ^{1}H NMR ($CDCl_3$): δ 1.21 (t, 3H, $J = 5.9$ Hz, CH_3), 2.53 (q, 2H, $J = 5.9$ Hz, CH_2), 3.63 (s, 2H, CH_2); 4.10 (s, 2H, NH_2); 6.54 (d, 2H, $J = 7.1$ Hz, Ar), 7.72 (d, 2H, $J = 7.1$ Hz, Ar). Anal. calcd. for $C_{10}H_{13}NOS$: c, 61.53; H, 6.67; S, 16.41. Found: C, 61.70; H, 6.94; S, 16.11.

I.R. Measurements—I.R. spectra were recorded at room temperature on a Perkin Elmer Model 283 grating spectrometer. The spectral width was 2.0 cm^{-1} in the carbonyl region.

The carbonyl frequencies were measured in the transmitance scale mode. For compounds (**1–7**) and (**9–16**) the *n*-hexane and chloroform solutions were ca. 1.0×10^{-2} M. A concentration of ca. 10^{-3} M was used for compound (**8**). Further dilution did not affect the spectra. Measurements were made using a pair of 1.00 mm sodium chloride matched cells. The spectra were calibrated with polystyrene at 1601.4 cm^{-1}. The carbonyl frequencies values for the more and less intense components of the doublet were accurated to ±0.5 and ±1 cm^{-1}, respectively.

The *cis/gauche* ratios for compounds (**1–8**) were obtained from the spectra recorded in the 1800–1600 cm^{-1} interval, in the absorbance scale mode. The *cis/gauche* relative concentrations were estimated from the ratio of the apparent molar absorptivities of the two components of the graphically decomposed bands,[21] assuming as an approximation equality of the molar absorptivities of the two rotamers. Due to the large ordinate scale expansion employed for compound (**8**), in *n*-hexane, the shoulder corresponding to the *cis* rotamer could be mislaid with the noise and therefore the carbonyl band was not decomposed. The estimated errors of the relative molar absorptivities are within 10%.

U.V. Measurements U.V. spectra were recorded on a Beckman model DK-2A spectrometer. Quartz matched cells of 1.00 cm pathway and spectrograde *n*-hexane were employed. For each substance, the spectra of three solutions of different concentrations ($10^{-2} - 10^{-4}$ M) were recorded, and ε_{max} for the bands assigned to the $n \rightarrow \pi^*$ transitions was estimated by linear regression of the absorbance against concentration. All the spectra were run at room temperature. For compounds (**8**) and (**16**) the band corresponding to the carbonyl $n \rightarrow \pi^*$ transition was not observed due to a complete overlap of the more intense benzene band.

NMR Measurements ^{13}C NMR spectra were recorded at 20 MHz using a Varian FT-80A spectrometer. The solutions contained in 0.5 mm o.d. tubes, were of 0.1 M in chloroform with 5% TMS as an internal reference. Experimental conditions were as follows: deuterium internal lock; temperature ca. 32°C; pulse width 5 μs; flip angle 20°; acquisition time 0.8 s; spectral width 5000 Hz; pulse repetition time, 1.3 s; number of data points 8192. The ^{13}C NMR spectra were recorded both in the proton noise decoupled and in the single frequency off-resonance decoupled mode. The chemical shifts were measured to an accuracy of 0.05 ppm.

^{1}H NMR spectra were recorded at 60 MHz on a Varian T-60 spectrometer in carbon tetrachloride or deuterochloroform and chemical shifts are reported with TMS as an internal standard.

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