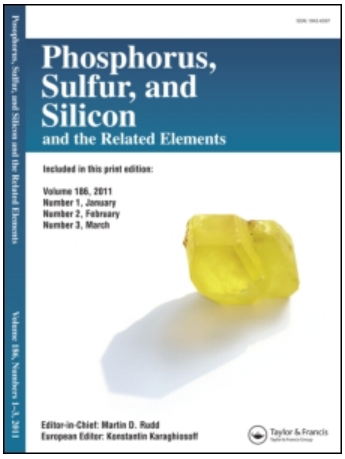

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Conformational And Electronic Interaction Studies Of 2-Seleno-Substituted Carbonyl Compounds And The Comparison With The 2-Thio-Analogues. XIII. α-Phenylseleno-*p*-Substituted Propiophenones[1]

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To cite this Article Olivato, Paulo R. , Filho, Rubens R. and Lopes, Julio C. D.(1994) 'Conformational And Electronic Interaction Studies Of 2-Seleno-Substituted Carbonyl Compounds And The Comparison With The 2-Thio-Analogues. XIII. α-Phenylseleno-*p*-Substituted Propiophenones[1]', Phosphorus, Sulfur, and Silicon and the Related Elements, 92: 1, 109 — 128
To link to this Article: DOI: 10.1080/10426509408021463
URL: http://dx.doi.org/10.1080/10426509408021463

Phosphorus, Sulfur, and Silicon, 1994, Vol. 92, pp. 109–128
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CONFORMATIONAL AND ELECTRONIC INTERACTION STUDIES OF 2-SELENO-SUBSTITUTED CARBONYL COMPOUNDS AND THE COMPARISON WITH THE 2-THIO-ANALOGUES. XIII. α-PHENYLSELENO-*p*-SUBSTITUTED PROPIOPHENONES[1]

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(Received May 19, 1994; in final form August 19, 1994)

The ν_{CO} IR analysis of α-phenylseleno-*p*-substituted propiophenones (I) indicates the existence of the *cis-gauche* rotational isomerism, the *gauche* conformer is predominant and the more polar one. The carbonyl frequency shifts for the *gauche* conformer of the title compounds are rather more negative than the $\Delta\nu_{CO}$ *gauche* shifts of the previously studied ω-phenylthio-*p*-substituted acetophenones (II). The title compounds (I) present practically no variation of the $\Delta\nu_{CO}$ absolute values on going from electron-donating to electron-attracting substituents in comparison to compounds of series (II) where this variation is significant. The Non Additivity Effect of the α-methyne carbon chemical shifts for series (I) is close to the NAE values of the α-methylene carbon for series (II). The bathochromic shifts of the $n \rightarrow \pi^*_{CO}$ transition for compounds of series (I) and (II) in relation to their parent compounds are quite close. The obtained data indicate an interplay of the π^*_{CO}/σ_{C-X}, π^*_{CO}/n_X and π_{CO}/σ^*_{C-X} orbital interactions which act on both series of compounds but in a larger extent for the selenium derivatives than for the sulfur derivatives. The π_{CO}/σ^*_{C-Se} interaction is the one which prevails in greater extent over the π_{CO}/σ^*_{C-S} interaction.

Key words: Conformational studies, electronic interactions, IR, ^{13}C NMR and UV spectroscopies, α-phenylseleno-*p*-substituted propiophenones.

INTRODUCTION

Previous studies from this laboratory by IR, UV, NMR and Electron Spectroscopies of some α-heterosubstituted ketones,[2,3,4] amides,[5,6] esters[7] and thioesters[8] showed that the π^*_{CO}/σ_{C-X} hyperconjugative interaction for their *gauche* rotamers is the main controlling factor of the *cis-gauche* rotational isomerism. However, our reports on some α-alkylthio-acetones and acetophenones and their *mono-* and *di*-oxygenated derivatives[9–13] along with the recent work on some ω-phenylthio-*p*-substituted acetophenones[14] suggested the simultaneous occurrence of the π^*_{CO}/σ_{C-S} and the π_{CO}/σ^*_{C-S} orbital interactions in the *gauche* rotamers of the title compounds. The high electron-affinity of the σ^*_{C-S} orbital has been indicated as responsible for the π_{CO}/σ^*_{C-S} orbital interaction in the α-thiosubstituted carbonyl compounds.

Taking into account that the σ_{C-Se} orbital should have lower ionization potential

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TABLE I

Frequencies and intensities of the carbonyl stretching bands in the infrared spectra of α-phenylseleno-*p*-substituted propiophenones X-ϕ-C(O)CH(CH_3)Seϕ

Compd.	X	n-C_6H_{14}			CCl_4						$CHCl_3$		
		ν^a	ε^b	$\varepsilon_c/\varepsilon_g{}^c$	ν	ε	$\varepsilon_c/\varepsilon_g$	ν^d	10ε	$\varepsilon_c/\varepsilon_g$	ν	ε	$\varepsilon_c/\varepsilon_g$
(1)	NH_2	-[e]	-	-	1681	73	0.22	-[f]			-		-
					1666	330		3317	30		1658	233	
(2)	OMe	1694	52	0.12	-		-	-		-			-
		1677	434		1672	365		3324	40		1665	396	
(3)	Me	1694	61	0.11	1687	37	0.07	-[f]	-	-	-		-
		1681	552		1676	530		3321	50		1670	373	
(4)	H	1688	93	0.23	-		-	-		-	-		-
		1683	404		1679	427		3339	50		1674	389	
(5)	Cl	1689	235	0.45	1686	98	0.20	3354	5	0.10	-		-
		1683	518		1679	501		3338	50		1674	412	
(6)	Br	1687	220	0.52	1687	90	0.20	3356	8	0.15	-		-
		1684	420		1680	445		3342	50		1674	412	
(7)	CN[g]	-		-	-		-	-		-	-		-
		1688	600		1684	532		3348	10		1680	497	

[a]In cm^{-1}. [b]Apparent molar absorptivity in $dm^3\ mol^{-1}\ cm^{-1}$. [c]Ratio of the higher and lower frequency components intensities of the analytically resolved band; subscripts c and g indicate cis and gauche rotamers respectively. [d]Maximum of the 1st overtone band (For details see Experimental Section). [e]The compound is practically insoluble in this solvent. [f]The very small intensity of the high frequency component precludes the analytical resolution of the band. [g]A single symmetric band is observed in all solvents.

than the σ_{C-S} orbital and that the σ^*_{C-Se} orbital should have higher electron affinity than the σ^*_{C-S} orbital, both the π^*_{CO}/σ_{C-Se} and π_{CO}/σ^*_{C-Se} orbital interactions in the α-seleno-carbonyl compounds might be stronger than the similar interactions which occur in the α-thio-carbonyl derivatives. So, it became of interest to study the α-phenylseleno-*p*-substituted propiophenones containing electron-attracting, hydrogen and electron donating-substituents by IR, ^{13}C NMR and UV spectroscopies. In analogy to our previous studies on some α-thiosubstituted acetophenones these compounds were chosen for the following reasons: the steric effect of the substituent directly linked to the carbonyl group (always an aryl group) is constant. Considering the possibility of the π^*_{CO}/σ_{C-Se} and π_{CO}/σ^*_{C-Se} orbital interactions in the *gauche* rotamers such interactions would be directly affected by varying the conjugation in the phenacyl group on going from electron-donating to electron-attracting substituents. This would affect the spectroscopic properties of such model compounds. The phenylselenopropiophenones were selected as their preparation is easier than the corresponding acetophenones.

RESULTS AND DISCUSSION

Cis-gauche Rotational Isomerism and Carbonyl Stretching Frequency Shifts

Table I shows the stretching frequencies, the corresponding apparent molar absorptivities of the analytically resolved bands and the ratios between the molar absorptivities of the higher and lower frequency components for the α-phenylseleno-*p*-substituted propiophenones **(1)–(7)**, in *n*-hexane, carbon tetrachloride (fundamental and 1st overtone transition) and in chloroform. Corresponding data for the parent propiophenones **(8)–(14)** are presented in Table II for comparison.

TABLE II

Carbonyl stretching frequencies[a] of *p*-substituted propiophenones X-ϕ-C(O)CH_2CH_3

Compd.	X	n-C_6H_{14}	CCl_4	$CHCl_3$
(8)	NH_2	-[b]	1681	1670
(9)	OMe	1694	1688	1679
(10)	Me	1696	1689	1684
(11)	H	1700	1694	1689
(12)	Cl	1700	1696	1689
(13)	Br	1700	1695	1689
(14)	CN	1704	1700	1694

[a]In cm^{-1}.

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

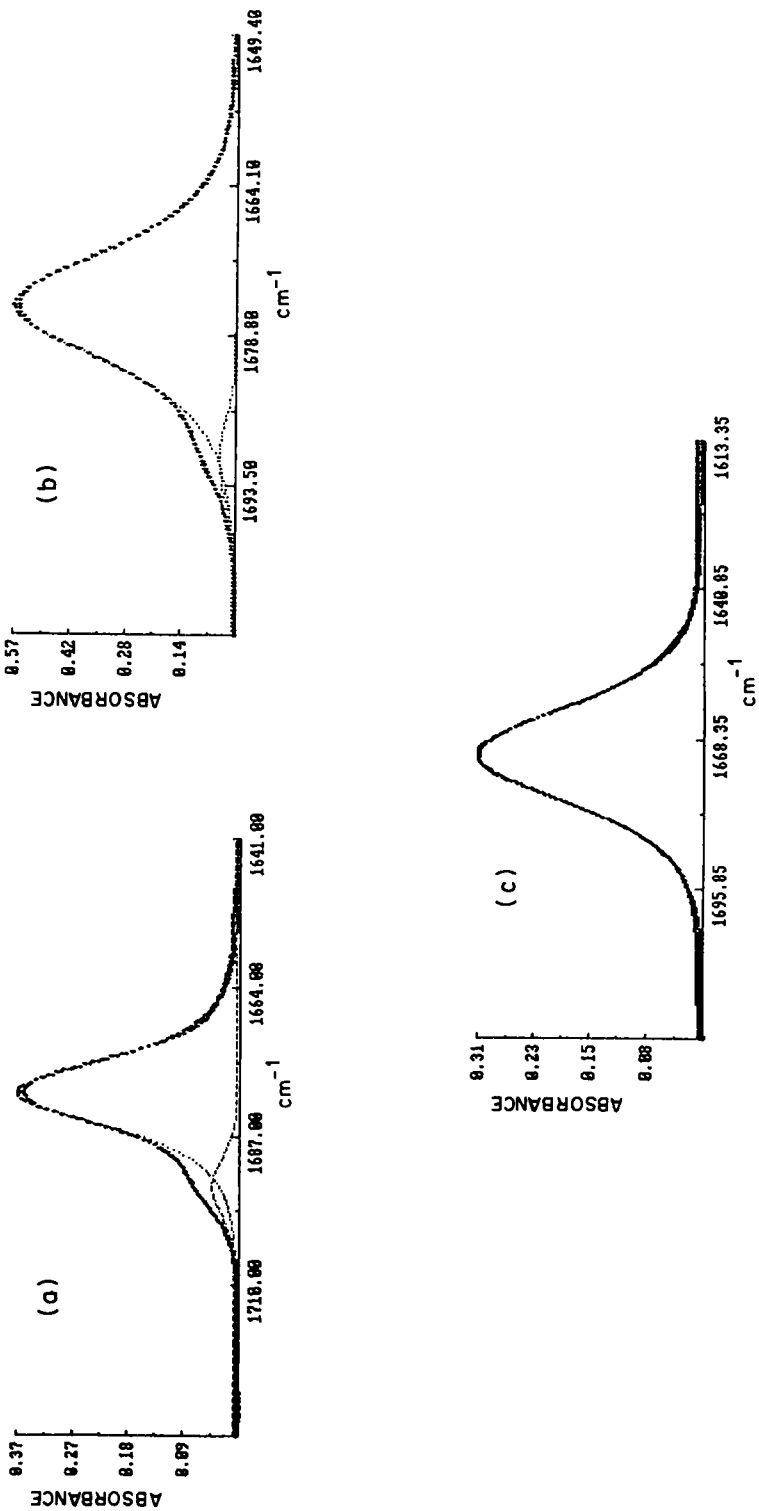


FIGURE 1 IR spectra of the α-phenylseleno-*p*-methylpropiophenone (3) showing the analytically resolved carbonyl stretching bands, in *n*-hexane (a), carbon tetrachloride (b), and chloroform (c). The experimental and the simulated spectra are practically superimposed.

The inspection of Table I shows that the title compounds in *n*-hexane exhibit two overlapped bands, except in compound (**7**) where only one band is observed. Compound (**1**) does not present any detectable band due to its very low solubility in this solvent. It should be noticed that in *n*-hexane the higher frequency component is a shoulder of the lower frequency component. Moreover, on going to carbon tetrachloride there is a decrease of the intensity or the disappearance of the higher frequency component of the doublet in relation to the lower one. When the solvent is chloroform only the lower frequency component is observed. Figure 1 illustrates this behavior. This solvent effect could be indicative of Fermi Resonance[15a] however, the occurrence of one or two bands in the first overtone region (in carbon tetrachloride) at frequencies approximately twice higher than those in the fundamental region and of close intensity ratios for compounds (**5**) and (**6**) rules out this possibility and strongly suggests the *cis-gauche* rotational isomerism.[16] It seems reasonable to suggest that the α-phenylselenopropiophenes may exist in three conformations i.e. one *cis* (**I**) and two *gauche* (**II** and **III**) (Figure 2) in analogy to our previous studies on α-(alkylthio)-thiopropionates[17] and -propionates.[18]

The inspection of Molecular Models indicates clearly that conformer *gauche* (**III**) is highly strained due to the sterically repulsion between the *gauche* methyl and selenophenyl groups and the *orto* hydrogen atom of the benzene ring. So, the *gauche* conformer (**III**) should be absent from the conformational equilibrium, and only the *cis* (**I**) and the *gauche* (**II**) conformers remain.

The increase of the solvent polarity decreases the intensity of the higher frequency band which corresponds to the *cis* (**I**) conformer, and simultaneously increases the intensity of the lower frequency band which corresponds to the *gauche* (**II**) conformer (see Table I and Figure 1). This trend indicates that the *gauche* conformer (**II**) is more polar than the *cis* (**I**). This behavior is in disagreement with the solvent effect generally observed in the heterosubstituted carbonyl compounds for which the *cis* rotamer was shown to be more polar than the *gauche* one.

This reversal of polarity in the α-phenylselenopropiophenones is supported by the carbonyl frequency shifts of the *cis* conformers ($\Delta\nu_c$), in comparison with the corresponding unsubstituted propiophenones (Table III). The $\Delta\nu_c$ values which

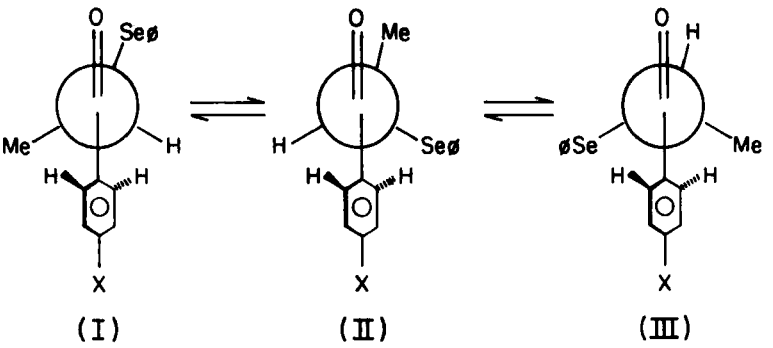


FIGURE 2 *Cis* (**I**) and *gauche* (**II** and **III**) conformations of α-phenylseleno-*p*-substituted propiophenones.

TABLE III

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

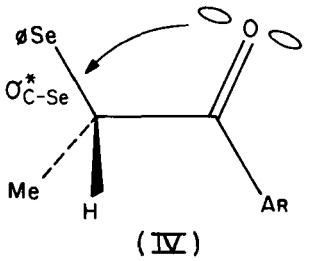
		n-C_6H_{14}		CCl_4		$CHCl_3$	
Compds.	Subst.	$\Delta\nu_c$	$\Delta\nu_g$	$\Delta\nu_c$	$\Delta\nu_g$	$\Delta\nu_c$	$\Delta\nu_g$
(1)-(8)	NH_2	-	-	0	-15	-	-12
(2)-(9)	OMe	0	-17	-	-16	-	-14
(3)-(10)	Me	-2	-16	-2	-13	-	-15
(4)-(11)	H	-12	-17	-	-15	-	-15
(5)-(12)	Cl	-11	-17	-10	-17	-	-15
(6)-(13)	Br	-13	-16	-8	-16	-	-15
(7)-(14)	CN	-	-17	-	-16	-	-14

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

should be positive due to the Repulsive Field Effect[15b] between the C=O and C–Se dipoles are negative in *n*-hexane and carbon tetrachloride.

In analogy to the α-thiosubstituted-thioesters[17] and -esters[18] the close spatial proximity of the α-selenium atom and the carbonyl group in the *cis* conformer suggests the occurrence of the $n_{O(CO)} \rightarrow \sigma^*_{C-Se}$ orbital interaction (Structure IV, Figure 3) and to a lesser extent the $\pi_{CO} \rightarrow 4d_{(Se)}$ orbital interaction, leading to a decrease in the carbonyl bond order and thus in its frequency. Such decrease of electronic density in the π_{CO} system should be also responsible for the decrease of the polarity of the *cis* conformer in relation to the *gauche* one (Structures V and VI, Figure 4).

The $\pi_{CO} \rightarrow$ nd orbital interaction should be less important for the α-seleno-



(IV)

FIGURE 3 *Cis* conformation of the α-phenylselenopropiophenones showing the $n_{O(CO)} \rightarrow \sigma^*_{C-Se}$ orbital interaction.

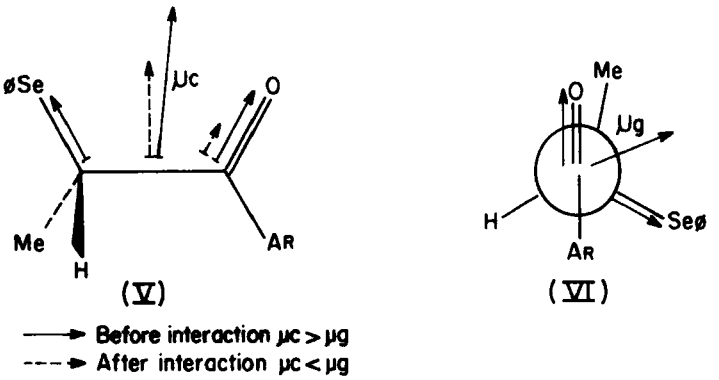


FIGURE 4 The variation of the polarity of the *cis* conformer in relation to that of the *gauche* one.

carbonyl compounds than it is for the α-sulfur-carbonyl compounds due to the higher energy of the $4d_{(Se)}$ orbital in relation to the $3d_{(S)}$ orbital.

Contrarily to what is observed in the α-phenylselenopropiophenones (Table III), the carbonyl *cis* shifts of the ω-phenylthio-*p*-substituted acetophenones are positive (Table IV). This difference in behavior may be justified by the fact that the electron-affinity of the σ^*_{C-Se} orbital (2.4 eV)[19] is 0.9 eV greater than the σ^*_{C-S} orbital (3.25 eV).[19] Thus, the $n_{O(CO)}$ lone pair energy level of the phenacyl group is closer to the σ^*_{C-Se} energy level than it is to the σ^*_{C-S} energy level. According to the Molecular Orbital Simple Perturbation Theory[20] this trend originates stronger $n_{O(CO)} \rightarrow \sigma^*_{C-Se}$ orbital interaction for the α-phenylselenopropiophenones than that occurring between the $n_{O(CO)}$ and σ^*_{C-S} orbitals for the ω-phenylthioacetophenones. This interaction originates a larger decrease in the carbonyl frequency of the *cis* rotamer for the selenium compounds than for the sulfur compounds. However, in the sulfur

TABLE IV

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

	CCl_4		$CHCl_3$	
X	$\Delta\nu_c$	$\Delta\nu_g$	$\Delta\nu_c$	$\Delta\nu_g$
OMe	+12	-6	+13	-2
H	+12	-7	+12	-3
NO_2	+10	-9	+15	-7

[a] $\Delta\nu_c$ and $\Delta\nu_g$ in cm^{-1}, refers to the difference: ν[X-ϕ-C(O)CH2Sϕ] - ν[X-ϕ-C(O)CH3].

[b] From reference 14.

derivatives the Repulsive Field Effect prevails over the $n_O \rightarrow \sigma^*_{C-S}$ orbital interaction leading to a positive carbonyl *cis* shifts in these compounds.

Table III shows that the mean carbonyl frequency shifts for the *gauche* rotamers ($\Delta\nu_g$) of the phenylselenopropiophenones are two or three fold more negative than the mean carbonyl frequency shifts for the *gauche* rotamers of the phenylthioacetophenones[14] (Table IV). This Table shows that there is a progressive increase in absolute value of the carbonyl *gauche* shifts for the phenylthioacetophenones on going from electron-donating to electron-attracting substituents. However in the case of the α-phenylselenopropiophenones there is not a significant variation of their carbonyl *gauche* shifts in the same direction i.e. the $\Delta\nu_g$ values are practically constant for the whole series. This different behavior between phenylthioacetophenones and phenylselenopropiophenones may be explained by the following considerations.

The V.B. theory states that for both series of compounds there is also the contribution of the hyperconjugative structure (**IX**) besides the Resonance structures (**VII**) and (**VIII**), which are present in the parent *p*-substituted acetophenones or propiophenones (Figure 5). This contribution increases as the conjugation between the *para*-substituent and the carbonyl group in the phenacyl group decreases. In fact the carbonyl frequency shifts presented in Table IV for the ω-phenylthio-*p*-substituted acetophenones are in line with these predictions.

The small carbonyl frequency shift observed for the *p*-methoxy compound is a consequence of the decrease in the carbonyl force constant, due to a smaller contribution of the hyperconjugative structure. The large frequency shift in the *p*-nitro compound 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 the orbital interactions based on the Molecular Orbital Simple Perturbation Theory.[20] In fact Figure 6a illustrates that the π^*_{CO} energy level, which is related to the LUMO of

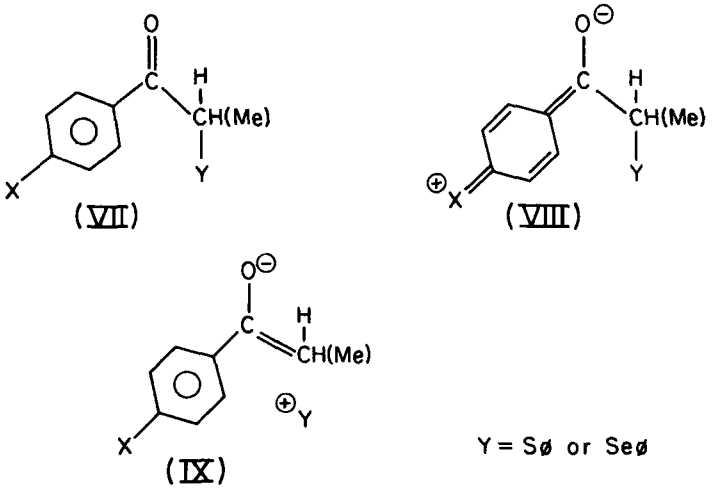


FIGURE 5 Resonance structures for the α-phenylthio-*p*-substituted acetophenones or for the α-phenylseleno-*p*-substituted propiophenones.

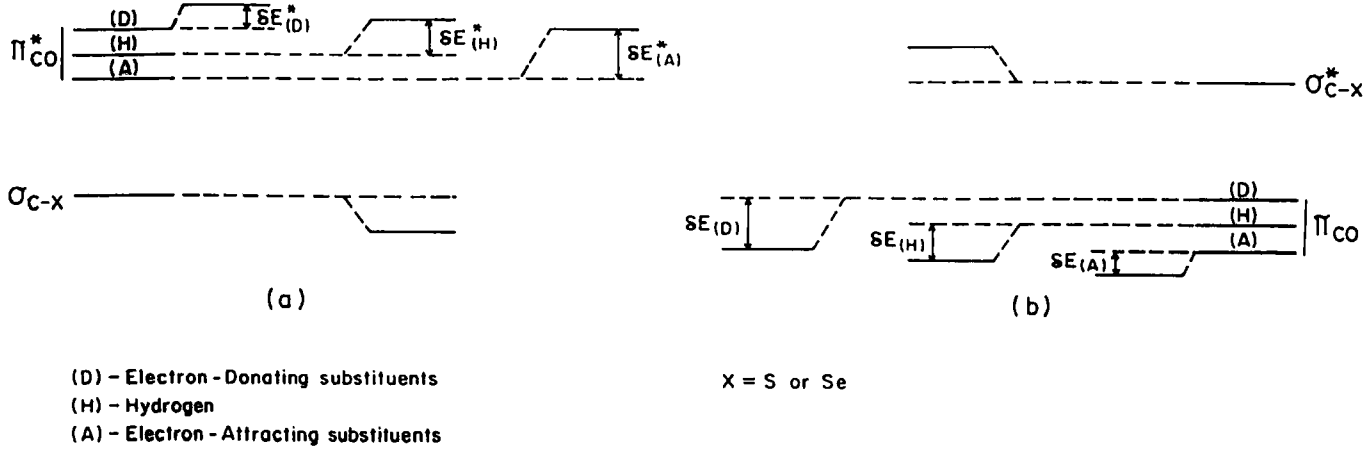


FIGURE 6 Qualitative energy level diagram showing the σ_{C-X}, π^*_{CO}, π_{CO}, σ^*_{C-X} orbitals of the α-phenylseleno- or α-phenylthio-*p*-substituted aromatic ketones before and after π^*_{CO}/σ_{C-X} (a) and π_{CO}/σ^*_{C-X} (b) orbital interactions.

the phenacyl group, in the *p*-substituted-acetophenones or propiophenones decreases progressively on going from electron-donating to electron-attracting substituents.[21,22] This trend originates stronger π^*_{CO}/σ_{C-X} hyperconjugative interaction as the $\pi^*_{CO}-\sigma_{C-X}$ orbital approximate to each other progressively in this direction.

The π^*_{CO} energy level of the phenacyl group is closer to the σ_{C-Se} energy level than the σ_{C-S} energy level due to the lower ionization potential of the σ_{C-Se} orbital (12.0 eV)[23] in relation to that of the σ_{C-S} orbital (12.68 eV).[23] Thus a greater contribution of the π^*_{CO}/σ_{C-X} hyperconjugative interaction for the α-seleno-carbonyl compounds than that for the corresponding α-thio-carbonyl compounds should be expected. Furthermore the σ_{C-X} energy level is close to the π^*_{CO} orbital of the phenacyl group bearing in *para* position electron-attracting substituents and further apart from the electron-donating substituents (Figure 6a).

Larger progressive contribution of the π^*_{CO}/σ_{C-X} hyperconjugative interaction (Structure IX, Figure 5) for the selenium compounds in relation to the corresponding sulfur compounds, on going from electron-donating to electron-attracting substituents should also be expected. This interaction should lead to a greater decrease in the carbonyl force constant and thus in its frequency for the selenium compounds than for the sulfur compounds, in the same direction. However, the π_{CO} energy level of the phenacyl group is closer to the σ^*_{C-Se} energy level than the σ^*_{C-S} energy level due to the higher electron-affinity of the σ^*_{C-Se} orbital (2.4 eV)[19] in relation to the σ^*_{C-S} orbital (3.3 eV).[19] Thus, a greater contribution of the π_{CO}/σ^*_{C-X} interaction for the α-seleno-carbonyl compounds than that for the corresponding α-thio-carbonyl compounds should be expected. Contrarily to the π^*_{CO}/σ_{C-X} hyperconjugation the π_{CO}/σ^*_{C-X} interaction is favored on going in the phenacyl group from electron-attracting to electron-donating substituents (Figure 6b). Electron-donating substituents push up the π_{CO} orbital energy level, which is related to the HOMO of the phenacyl group,[11,21,22] approximating it to the σ^*_{C-X} orbital thus facilitating the π_{CO}/σ^*_{C-X} orbital interaction. While electron-attracting substituents stabilize the π_{CO} orbital level making the π_{CO}/σ^*_{C-X} orbital interaction more difficult. From the above arguments a larger progressive contribution of the π_{CO}/σ^*_{C-X} orbital interaction for the α-phenylselenopropiophenones in relation to the ω-phenylthioacetophenones, on going from electron-attracting to electron-donating substituents should be expected. This interaction should lead to a greater decrease in the carbonyl force constant and thus in its frequency for the selenium compounds than for the sulfur compounds in the same direction.

The energy gap between σ^*_{C-Se} (2.4 eV)[19] and σ^*_{C-S} (3.25 eV)[19] orbitals is 0.9 eV and the energy gap between the σ_{C-Se} (12.0 eV)[23] and σ_{C-S} (12.68 eV)[23] orbitals is 0.7 eV. Consequently the π_{CO}/σ^*_{C-Se} interaction should predominate over the π_{CO}/σ^*_{C-S} interaction in a greater extent than the π^*_{CO}/σ_{C-Se} interaction prevails over the π^*_{CO}/σ_{C-S} interaction. It may be concluded that the observed progressive increase in the negative carbonyl *gauche* shifts of the ω-phenylthioacetophenones (Table IV) on going from electron-donating to electron-attracting substituents ascribed mainly to π^*_{CO}/σ_{C-S} hyperconjugative interaction should be masked in the case of the α-phenylselenopropiophenones. In fact the π_{CO}/σ^*_{C-X} interaction acts in opposite direction increasing the negative carbonyl *gauche* shifts on going from electron-attracting to electron-donating substituents and is more pronounced for the selenium compounds than for the sulfur compounds. Therefore the practically

constant carbonyl *gauche* shifts observed in Table III for the α-phenylselenopropiophenones series are in line with this analysis.

The n_{Se} lone pair ionization energy (8.40 eV)[23] is lower than that of the n_S lone pair (8.71 eV)[23] by ca. 0.3. eV and is closer to the empty π^*_{CO} orbital. This trend leads to a larger π^*_{CO}/n_{Se} superjacent orbital interaction[24] than the π^*_{CO}/n_S one (Figure 7). This interaction operates in the *gauche* rotamer of the α-heterosubstituted carbonyl compounds between the non-bonding electron pair (n_X) and the low-lying π^*_{CO} (Structure X, Figure 8).

The summing up of the π^*_{CO}/σ_{C-X}, π_{CO}/σ^*_{C-X} and π^*_{CO}/n_X orbital interactions favours the α-seleno-carbonyl compounds in a greater extent than the α-thio-carbonyl compounds, leading to a larger decrease in the carbonyl force constants and thus in the frequencies of the α-phenylseleno-*p*-substituted propiophenones than in the frequencies of the ω-phenylthio-*p*-substituted acetophenones in relation to their parent compounds, as observed in Tables III and IV.

Furthermore all the above mentioned orbital interactions are two-electron stabilizing[24] and are responsible for the high stability of the *gauche* rotamers of the α-seleno-carbonyl compounds leading to their great predominance over the *cis* ones.

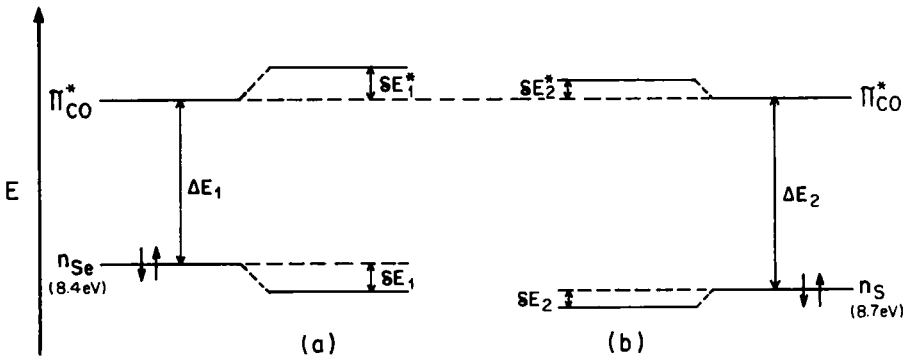
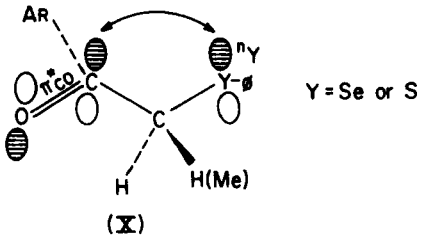


FIGURE 7 Qualitative energy level diagram for the π^*_{CO}, n_{Se} and n_S orbitals showing the larger stabilization of the n_{Se} orbital due to the π^*_{CO}/n_{Se} superjacent interaction in α-seleno-carbonyl compounds (a) in relation to the stabilization of the n_S orbital due to the π^*_{CO}/n_S superjacent interaction in α-thio-carbonyl compounds (b).



(X)

FIGURE 8 Superjacent interaction between the n_Y lone pair and the low-lying π^*_{CO} orbital in the *gauche* rotamers for the α-phenylseleno- and α-phenylthio aromatic ketones.

Carbon-13 NMR Chemical Shifts

Table V shows the ^{13}C NMR data for the methyne carbon (in—C(O)CH group), for the carbonyl carbon of the α-phenylseleno-*p*-substituted propiophenones (**1**)–(**7**), and the data for the methylene carbon and for the carbonyl carbon of the parent *p*-substituted propiophenones (**8**)–(**14**). This Table presents the calculated α-methyne carbon for the α-selenopropiophenones along with the Non Additivity Effect[25] (NAE) i.e. the difference between the experimental and the calculated α-methyne carbon chemical shifts.

It is well known that the variation on conjugation in the carbonyl group in the

TABLE V

^{13}C NMR chemical shifts[a] for the methyne (in CHCO—), methylene (in —CH_2CO—) and carbonyl carbons of the propiophenones X-ϕ-C(O)CH(CH_3)Y, in $CDCl_3$, and the α effect of the X-ϕC(O)-group

		Y = Seϕ			Y = H			
X	Compd.	δ_{CO}	δ_{CH}	$\Delta\delta^b_{CH}$	Compd.	δ_{CO}	δ_{CH_2}	α^cX-ϕ-C(O)-
NH_2	(1)	195.14	39.48 46.3[d]	-6.6	(8)	199.13	30.90	25.2
OMe	(2)	195.02	39.42 47.0	-.7.6	(9)	200.60	31.55	25.9
Me	(3)	195.77	39.43 46.7	-7.3	(10)	200.01	31.25	25.6
H	(4)	196.05	39.48 46.9	-7.4	(11)	200.43	31.45	25.8
Cl	(5)	194.72	39.44 47.3	-7.9	(12)	198.84	31.90	26.2
Br	(6)	194.82	39.40 46.9	-7.5	(13)	199.33	31.48	25.8
CN	(7)	194.15	39.72 47.3	-7.6	(14)	199.01	31.87	26.2

[a]In ppm relative to TMS.

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

[c]See text.

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

p-substituted aromatic ketones does not affect significantly the shielding effect on the carbonyl carbon. In fact a practically constant carbonyl carbon chemical shifts for both series of propiophenones (**1**)–(**7**) and (**8**)–(**14**) on going from electron-attracting to electron-donating substituents can be noticed in Table V. This Table shows practically constant upfield shift of ca. 4.3 ppm for the carbonyl carbon of the α-seleno derivatives in relation to their parent compounds, which may be attributed to the inductive effect of the α-phenylseleno group (σ_I = 0.31).[26] As for ω-phenylthio-*p*-substituted acetophenones (Table VI) almost the same upfield shift of ca. 4.0 ppm has been observed in relation to their parent acetophenones for which the inductive effect of the α-phenylthio group (σ_I = 0.28)[26] is almost the same of the α-phenylseleno group.

The computed α-methyne carbon chemical shifts[27] for the α-phenylselenopropiophenones may be obtained from Equation 1, where $\alpha_{Se\phi}$ and $\alpha_{X\text{-}\phi C(O)}$ are the α effects of the phenylseleno- and the phenacyl groups whereas 5.7 is the chemical shift of the ethane carbon.

$$\delta_{CH} = 5.7 + \alpha_{X\text{-}\phi C(O)} + \alpha_{Se\phi} \quad (1)$$

The $\alpha_{X\text{-}\phi C(O)}$ and $\alpha_{Se\phi}$ effects may be obtained from Equations (2) and (3) i.e. from the α-methylene carbon chemical shifts of the propiophenones or from the α-methylene carbon chemical shift of the ethylphenylselenide and the chemical shift of the ethane.

$$\alpha_{X\text{-}\phi C(O)} = \delta_{CH_2}[X\text{-}\phi\text{-}C(O)\underline{C}H_2CH_3] - 5.7 \quad (2)$$

$$\alpha_{Se\phi} = \delta_{CH_2}[\phi Se\underline{C}H_2CH_3] - 5.7 \quad (3)$$

As the α-methylene carbon chemical shift for the ethylphenylselenide in chloroform is 21.08 ppm, the α-effect of the Seϕ group is 15.37 ppm.

TABLE VI

Non Additivity Effect ($\Delta\delta$)[a,b] of the α-methylene carbon chemical shifts and the difference between the carbonyl carbon chemical shifts[c] of some ω-phenylthio-*p*-substituted acetophenones[d] X-ϕ-C(O)$CH_2S\phi$ and their parent acetophenones, X-ϕ-C(O)CH_3, in $CDCl_3$

X	$\Delta\delta_{CH_2}$	$\Delta\delta_{CO}$
OMe	-7.10	-4.1
H	-7.12	-4.1
NO_2	-7.38	-3.8

[a] In ppm.

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

[c] $\Delta\delta_{CO} = \delta_{CO[X\text{-}\phi\text{-}C(O)CH_2S\phi]} - \delta_{CO[X\text{-}\phi\text{-}C(O)CH_3]}$

[d] From ref. 14.

The calculated α effect of the X-ϕC(O)— group for the whole propiophenone series is practically constant i.e. ca. 25.7 ppm (see Table V).

Additionally, the experimental chemical shifts for the α-methyne carbon of the α-phenylselenopropiophenones (**1**)–(**7**) are upfield in relation to the computed values by ca. 7.4 ppm (mean value for the whole series). This Non Additivity effect value is very close to that previously noticed[14] for the α-methylene carbon of the ω-phenylthioacetophenones series whose mean value is ca. 7.2 ppm (Table VI).

In analogy to what has been proposed by Nesmeyanov[28] the additional shielding on the α-methyne carbon i.e. the Non Additivity Effect in the α-phenylselenopropiophenones may be ascribed to an increase in the double bond character between the α-methyne and the carbonyl carbons due to the π^*_{CO}/σ_{C-Se} hyperconjugative interaction.

The quasi-equal NAE for the α-methyne and α-methylene carbon chemical shifts for the phenylselenopropiophenones and phenylthioacetophenones respectively seems to indicate that their *gauche* rotamers should have practically the same α-methyne (or methylene) carbon—carbonyl carbon double bond character (bond order).

As outlined in the preceding section the σ_{C-Se} orbital has a lower ionization energy than the σ_{C-S} orbital by ca. 0.7 eV. The π^*_{CO}/σ_{C-X} hyperconjugative interaction and consequently the additional shielding on the α-carbon i.e. the Non Additivity Effect should contribute for the α-seleno-ketones in a larger degree than for the α-thio-ketones. Moreover the n_{Se} lone pair has a lower ionization energy than the n_S lone pair by ca. 0.3 eV. The π^*_{CO}/n_X superjacent interaction[4,24] may cause an increase in the electron density on the α-carbon atom and therefore an additional shielding on it i.e. the NAE should also be more pronounced for the selenium compounds than for the sulfur compounds.

In agreement with our previous studies[8–14] the π_{CO}/σ^*_{C-X} interaction leads to a decrease in the Non Additivity Effect on the α-carbon favouring the selenium compounds in relation to the sulfur compounds as the σ^*_{C-Se} orbital has a higher electron-affinity than the σ^*_{C-S} orbital by ca. 0.9 eV. Both the π^*_{CO}/σ_{C-X} and π^*_{CO}/n_X orbital interactions favour the increasing shielding of the α-carbon atom in the α-seleno-ketones in relation to the α-thio-ketones and are virtually counterbalanced by the π_{CO}/σ^*_{C-X} interaction which is predominant for the α-seleno-ketones in comparison to the α-thio-ketones. Thus, the very similar NAE of α-methyne and α-methylene carbon chemical shifts for both α-phenylselenopropiophenones and α-phenylthioacetophenones series is explained (see Tables V and VI).

Carbonyl $n \rightarrow \pi^*$ Transition Energies and Intensities

Table VII shows the wavelengths and the molar absorptivities of the $n \rightarrow \pi^*$ carbonyl bands for the propiophenones (**9**)–(**14**) and for the corresponding α-phenylselenopropiophenones (**2**)–(**7**), in *n*-hexane. Table VIII shows the corresponding UV data for some acetophenones and for the corresponding ω-phenylthioacetophenones in *n*-hexane, for comparison.

Inspection of Tables VII and VIII shows that the introduction of a phenylselenyl- and phenylthio-groups in the α position of the *p*-substituted propiophenones and acetophenones respectively results in bathochromic shifts of ca. 20 nm for the

selenium derivatives and of ca. 25 nm for the sulfur derivatives followed by an intensification of ca. 20 fold for the selenium derivatives and of ca. 10 fold for the sulfur derivatives.

The bathochromic shift of the $n \rightarrow \pi^*$ transition may be explained on the grounds of the hyperconjugative interaction between the σ^*_{C-X} and π^*_{CO} empty orbitals in the *gauche* rotamers of the title compounds leading to the stabilization of the π^*_{CO} orbital and therefore to a smaller $n \rightarrow \pi^*$ energy gap.

The σ^*_{C-Se} orbital has higher electron-affinity than the σ^*_{C-S} orbital (see preceding section) approximating the π^*_{CO} energy level to the σ^*_{C-Se} energy level more than to the σ^*_{C-S} energy level. This trend should originate stronger $\pi^*_{CO}/\sigma^*_{C-X}$ hyperconjugative interaction for the α-seleno-carbonyl compounds than for the α-thio-carbonyl compounds. However, this prediction is in disagreement with the experimental data. Slightly smaller bathochromic shifts of the $n \rightarrow \pi^*$ transition are observed for the α-seleno-carbonyl compounds ($\Delta\lambda \cong 20$ nm) in comparison to the α-thio-carbonyl compounds ($\Delta\lambda \cong 25$ nm) (Tables VII and VIII) instead of

TABLE VII

U.V. data for the carbonyl $n \rightarrow \pi^*$ transition of the propiophenones $X\text{-}\phi C(O)CH(CH_3)Y$, in *n*-hexane

		Y = H			Y = Seϕ		
X	Compd.	λ[a,b]	ε[c]	Compd.	λ	ε	Δλ[d]
OMe	(9)	315	12	(2)	333	382	18
Me	(10)	310 321	63 66	(3)	327 338	373 380	16
H	(11)	315 321	17 17	(4)	328 338 350	606 598 485	20
Cl	(12)	315 323	53 53	(5)	331 341	1118 1172	17
Br	(13)	315 323	62 62	(6)	331 341	972 1016	17
CN	(14)	322 333	76 76	(7)	344 352 361	1035 1110 940	24

[a] λ in nm.

[b] Maximum of the vibrational contour.

[c] Apparent molar absorptivity in $dm^3\ mol^{-1}\ cm^{-1}$.

[d] Δλ, refers to the difference of the maxima mean value of the vibrational contour for: λ(α-phenylseleno-p-substituted propiophenone) - λ(parent propiophenone).

TABLE VIII

U.V. data for the carbonyl n → π^* transition of some acetophenones X-ϕC(O)CH_2Y,[a] in *n*-hexane

	Y = H		Y = Sϕ		
X	λ[b]	ε[c]	λ	ε	Δλ[d]
OMe	310	97	333	762	23
H	317	43	340	555	23
NO_2	325	288	357	676	32

[a]From ref. 14.

[b]Maximum of the vibrational contour.

[c]Apparent molar absorptivity in $dm^3\ mol^{-1}\ cm^{-1}$.

[d]Δλ refers to the difference:

$\lambda_{(\omega\text{-phenylthio-p-substituted acetophenone})} - \lambda_{(\text{parent acetophenone})}$.

the expected larger bathochromic shifts of the n → π^*_{CO} transition for the selenium compounds in relation to the sulfur compounds, on going from the unsubstituted aromatic ketones to the α-phenylseleno and α-phenylthio derivatives. This unexpected behavior is partially explained in Figure 9, as the equality of the unperturbed π_{CO} energy levels for both α-seleno- and α-thio-carbonyl compounds was assumed. The π_{CO}/σ^*_{C-Se} interaction is stronger than the π_{CO}/σ^*_{C-S} interaction leading to a larger destabilization of the σ^*_{C-Se} energy level (δE^*_{Se}) than the destabilization of the σ^*_{C-S} energy level (δE^*_S).

The π_{CO}/σ^*_{C-X} orbital interaction still leaves the π^*_{CO} level closer to the σ^*_{C-Se} than to the σ^*_{C-S} level but in a lesser extent.

This should yet originate a smaller n → π^* energy gap for the selenium compounds (ΔE_1) in relation to the sulfur compounds (ΔE_2). However as the ionization energy of the σ_{C-Se} orbital (12.0 eV)[23] is lower than the ionization energy of the σ_{C-S} orbital (12.68 eV),[23] the repulsive four-electron π_{CO}/σ_{C-X} interaction pushes the π_{CO} energy level of the selenium compounds up in a greater extent than the π_{CO} level of the sulfur compounds (Figure 10).

Previous to π_{CO}/σ^*_{C-X} interaction the π_{CO} energy level of the selenium compounds was assumed to be equal to the sulfur compounds (Figure 9), however the π_{CO} energy level for the selenium compounds is higher than for the sulfur compounds as shown in Figure 10. This trend approximates even more the $\pi_{CO} - \sigma^*_{C-Se}$ than the $\pi_{CO} - \sigma^*_{C-S}$ energy levels so that the σ^*_{C-Se} and the σ^*_{C-S} energy levels are closer to each other after the π_{CO}/σ^*_{C-X} interaction. Consequently after the $\pi^*_{CO}/\sigma^*_{C-X}$ hyperconjugative interaction practically the same bathochromic shifts for the n → π^*_{CO} energy transitions for the α-phenylselenopropiophenones and for the α-phenylthioacetophenones in relation to their parent compounds can be expected as observed in Tables VII and VIII.

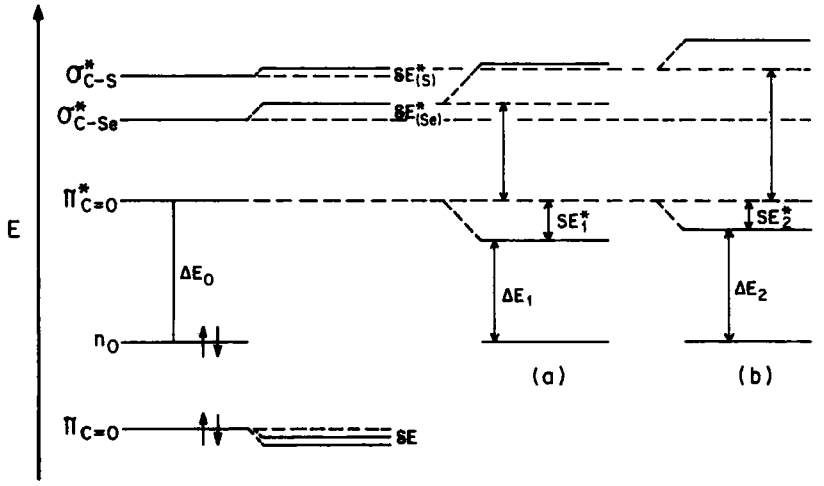


FIGURE 9 Qualitative energy level diagram of the π_{CO}, n_O, π^*_{CO}, σ^*_{C-Se} and σ^*_{C-S} orbitals for the *gauche* rotamers of the α-seleno- (a) and α-thio-carbonyl (b) compounds showing the larger destabilization of the σ^*_{C-Se} orbital (δE^*_{Se}) in relation to the σ^*_{C-S} orbital (δE^*_S) due to the π_{CO}/σ^*_{C-X} interaction. It shows the apparent slight bathochromic shift for the $n \rightarrow \pi^*_{CO}$ transition (ΔE_1) for (a) in relation to that (ΔE_2) for (b).

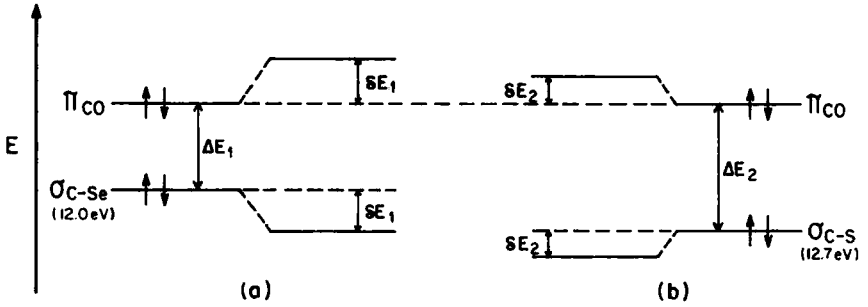


FIGURE 10 Qualitative energy level diagram for the π_{CO}, σ_{C-Se} and σ_{C-S} orbitals showing the larger destabilization (δE_1) for the π_{CO} orbital due to the σ_{C-Se}/π_{CO} interaction in the *gauche* rotamers of the α-seleno-carbonyl compounds (a) in relation to the smaller destabilization (δE_2) for the π_{CO} orbital due to the σ_{C-S}/π_{CO} interaction in the *gauche* rotamers of the α-thio-carbonyl compounds (b).

EXPERIMENTAL

Materials

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

Propionyl chloride, acetanilide, *n*-butil lithium in *n*-hexane, tetrahydrofuran, diisopropylamine, diphenyl diselenide were commercial products. Commercial propiophenone (**11**), *p*-methyl- (**10**), *p*-methoxy- (**9**) propiophenones were purified by distillation. Commercial *p*-chloro- (**12**) and *p*-bromo- (**13**) propiophenones were purified by recrystallization from ethanol (95%). *p*-Aminopropiophenone[29] (**8**) was prepared by a literature procedure. *p*-Cyanopropiophenone (**14**) was obtained by an adaptation of the *p*-tolyl cyanide preparation i.e. by the reaction of the neutralized solution of the sodium diazonium salt of the *p*-aminopropiophenone with copper (I) cyanide solution. A crude solid was collected after steam destillation. Recrystallization from ethanol yielded a white solid with M.P. 53.5–56° (Lit.[31] = 54–55°).

The α-phenylseleno-*p*-substituted propiophenones X-φC(O)CH(CH_3)Seφ were obtained following the Reich's procedure[32] described for the preparation of α-phenylselenopropiophenone (**4**). After the solvent evaporation the crude oil was purified by a preparative silica gel layer chromatography using as eluent 1:1 benzene *n*-hexane solution. The *p*-amino- (**1**) and *p*-cyano- (**7**) derivatives were the only products which crystallized after the chromatography. It was not possible to crystallize the other α-phenylselenopropiophenones as they decompose when submitted to vacuum distillation at 0.05 Torr. So, the whole α-phenylselenopropiophenones except the amino- (**1**) and the cyano (**7**) derivatives were used without further purification after the elimination of solvent traces under 0.05 Torr at room temperature during 2–3 h.

The following α-phenylseleno-*p*-substituted propiophenones were prepared by the Reich's method:

α-phenylseleno-p-aminopropiophenone (**1**): orange solid (yield 48%), m.p. 168.5–172°C, (new compound); ^{1}H NMR ($CDCl_3$): δ 1.61 (d, 3H, J = 6.9 Hz), 4.27 (bs, 2H, NH_2); 4.65 (q, 1H, J = 6.9 Hz); 7.21–7.81 (m, 9H, Ar, Seφ). Anal. Calcd. for $C_{15}H_{15}NOSe$: C, 59.22; H, 4.97; N, 4.60. Found: C, 59.04; H, 5.03; N 4.61.

α-phenylseleno-p-methoxypropiophenone (**2**): orange oil (yield 64%), (new compound); ^{1}H NMR ($CDCl_3$): δ 1.57 (d, 3H, J = 6.9 Hz), 3.84 (s, 3H, CH_3O); 4.60 (q, 1H, J = 6.9 Hz); 6.83–7.92 (m, 9H, Ar, Seφ). Anal. Calcd. for $C_{16}H_{16}O_2Se$: C, 60.19; H, 5.05. Found: C, 60.58; H, 5.32.

α-phenylseleno-p-methylpropiophenone (**3**): yellowish oil (yield 54%), ^{1}H NMR ($CDCl_3$): δ 1.62 (d, 3H, J = 7.0 Hz), 2.39 (s, 3H, CH_3); 4.65 (q, 1H, J = 7.0 Hz) 7.10–7.92 (m, 9H, Ar, Seφ). Lit.[33] ^{1}H NMR ($CDCl_3$): δ 1.64 (d, 3H, J = 7 Hz); 2.41 (s, 3H, CH_3); 4.67 (q, 1H, J = 7 Hz); 7.15–7.96 (m, 9H). Anal. Calcd. for $C_{16}H_{16}OSe$: C, 63.27; H, 5.32. Found: C, 63.60; H, 5.46.

α-phenylselenopropiophenone (**4**): yellowish oil (yield 57%), (Lit.[32] 36.5–37°C); ^{1}H NMR ($CDCl_3$): δ 1.62 (d, 3H, J = 6.7 Hz), 4.66 (q, 1H, J = 6.8 Hz); 7.20–7.90 (m, 10H, Ar, Seφ). Anal. Calcd. for $C_{15}H_{14}OSe$: C, 62.29; H, 4.88. Found: C, 61.91; H, 5.39.

α-phenylseleno-p-chloropropiophenone (**5**): yellowish oil (yield 45%); (new compound); ^{1}H NMR ($CDCl_3$): δ 1.62 (d, 3H, J = 6.8 Hz); 4.63 (q, 1H, J = 6.8 Hz); 7.25–7.82 (m, 9H, Ar, Seφ). Anal. Calcd. for $C_{15}H_{13}ClOSe$: C, 55.66; H, 4.05. Found: C, 56.02; H, 4.00.

α-phenylseleno-p-bromopropiophenone (**6**): yellowish oil (yield 47%); ^{1}H NMR ($CDCl_3$): δ 1.60 (d, 3H, J = 6.8 Hz), 4.56 (q, 1H, J = 6.8 Hz); 7.23–7.72 (m, 9H, Ar, Seφ). Lit.[33] ^{1}H NMR ($CDCl_3$): δ 1.64 (d, 3H, J = 7 Hz), 4.59 (q, 1H, J = 7 Hz); 7.12–7.80 (m, 9H). Anal. Calcd. for $C_{15}H_{13}BrOSe$: C, 48.94; H, 3.56. Found: C, 49.27; H, 3.66.

α-phenylseleno-p-cyanopropiophenone (**7**): yellow solid (yield 51%); m.p. = 100.1–102.9°C (new compound); ^{1}H NMR ($CDCl_3$): δ 1.65 (d, 3H, J = 6.9 Hz); 4.62 (q, 1H, J = 6.8 Hz); 7.22–7.40 (m, 5H, Seφ). 7.69 (d, 2H, J = 6.0 Hz, Ar), 7.92 (d, 2H, J = 6.0 Hz, Ar). Anal. Calcd. for $C_{16}H_{13}NOSe$: C, 61.10; H, 4.14; N, 4.45. Found: C, 61.06; H, 4.22; N, 4.64.

I.R. Measurements

The conditions for recording the I.R. carbonyl stretching bands in both fundamental (1750–1620 cm^{-1}) and in the first overtone (3600–3200) regions for 1.0–3.0 × 10^{-2} $mol.dm^{-3}$ solutions of the α-phenylseleno-*p*-substituted propiophenones (**1**)–(**7**) as well as of the parent *p*-substituted propiophenones (**8**)–(**14**), in *n*-hexane, carbon tetrachloride and chloroform, using 0.5 mm sodium chloride and 1.00 cm quartz matched cells, respectively, have already been described.[4] The overlapped carbonyl stretching bands were deconvoluted computationally as previously described.[8,34]

For evaluation of the accuracy of the band envelope fit the root mean square of the residuals (DIS) was used. All the carbonyl bands analysed showed DIS values less than 0.50 percent of transmittance. The program was run on a IBM-PC/XT compatible computer. The very small intensity of the higher frequency component of the doublet in the first overtone region for the whole series except for compounds (**5**) and (**6**), precludes the analytical resolution of the overlapped band.

The carbonyl frequencies are accurate in the fundamental and in the first overtone regions to ±0.5 and ± 1 cm^{-1}, respectively.

The *cis/gauche* ratios for the α-phenylseleno-*p*-substituted propiophenones (**1**)–(**7**) were estimated from the absorbances ratio of the two components of the computationally resolved bands measured directly at their absorption maxima assuming equality of the molar absorption coefficients of the two rotamers.

NMR Spectra

The ^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. sample tubes, were recorded at 200 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 μs; acquisition time, 2.7 s; spectral width, 602.4 Hz; pulse repetition time 0.0 s; number of transients, 100; and number of data points, 32 K. Similarly, for the ^{13}C NMR spectra: pulse width, 2.0 μs; acquisition time; 1.3 s, spectral width 12.500 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.

UV Spectra

The UV spectra of 10^{-3} – 10^{-4} mol.dm^{-3} solutions in *n*-hexane using a pair quartz matched cells of 1.00 cm pathway were recorded in a Hitachi U-2000 spectrometer.

ACKNOWLEDGEMENTS

The authors thank the Fundação de Amparo à Pesquisa do Estado de São Paulo and PADCT for financial support of this research and Conselho Nacional de Pesquisa for a scholarship (to R.R.F.) and for a grant (to P.R.O. and J.C.D.L.).

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