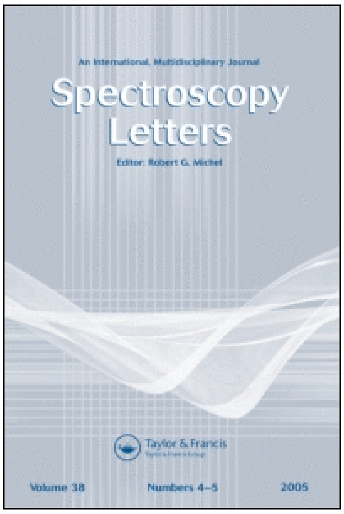

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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Paulo R. Olivato[a]; Sandra A. Guerrero[a]; Mario L. T. Hiu[a]; Janaina Mattos[a]; Simone Harms[a]; Marcos S. V. Schimidt[a]; Roberto Rittner[b]
[a] Instituto de Química, Universidade de São Paulo, São Paulo, S.P., Brazil [b] Instituto de Química, Universidade Estadual de Campinas, Campinas, S.P., Brazil

To cite this Article Olivato, Paulo R. , Guerrero, Sandra A. , Hiu, Mario L. T. , Mattos, Janaina , Harms, Simone , Schimidt, Marcos S. V. and Rittner, Roberto(1999) 'Conformational and Electronic Interaction Studies of *P*-Substituted α-Phenoxyacetones', Spectroscopy Letters, 32: 6, 1041 — 1056

To link to this Article: DOI: 10.1080/00387019909350049

URL: http://dx.doi.org/10.1080/00387019909350049

SPECTROSCOPY LETTERS, 32(6), 1041–1056 (1999)

CONFORMATIONAL AND ELECTRONIC INTERACTION STUDIES OF *p*-SUBSTITUTED α-PHENOXYACETONES

Key words: Conformational analysis, Electronic interaction, α-Phenoxyacetones

Paulo R. Olivato*[,a], Sandra A. Guerrero[a], Mario L.T. Hiu[a], Janaína Mattos[a], Simone Harms[a], Marcos S.V. Schimidt[a] and Roberto Rittner[b].

[a]Instituto de Química, Universidade de São Paulo, Caixa Postal 26.077, 05599-970, São Paulo, S.P., Brazil;
[b]Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13083-970, Campinas, S.P., Brazil.

ABSTRACT

The ν_{CO} analysis of p-substituted α-phenoxy-acetones X-ϕ-O-CH_2-C(O)-Me (**1**-**6**) indicates the existence of the *cis*/*gauche* rotational isomerism. The nearly constant increase in the *cis*/*gauche* population ratios for the whole series, on going from carbon tetrachloride to acetonitrile, and the small sensitivity of the carbonyl frequency shifts ($\Delta\nu_C$) for the *cis* rotamer,

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*The corresponding author

on going from electron-attracting to electron-donating substituents, are interpreted as an interplay of the Field (F) and the Inductive (-I) Effects, which originates an almost constant carbonyl bond order, and suggests that the *cis* rotamers have almost the same energy in the whole series. The decrease in the *cis/gauche* population ratios, in all solvents, and the deshielding effects on the carbonyl carbon atom, and on the methylene carbon atom in a weaker extent, observed in the ^{13}C NMR spectra, on going from electron-attracting to electron-donating substituents, are *discussed in terms of* π^*_{CO}/n_O *orbital and* $Ar^{\delta+}$-$O^{\delta-}$ ---- $C^{\delta+}$=$O^{\delta-}$ Coulombic interactions, which stabilize the *gauche* rotamers of the investigated compounds.

INTRODUCTION

Our previous reports on some aliphatic α-heterosubstituted carbonyl compounds (acetones, acetophenones, thioesters, esters and amides)[1,2] have suggested that the $\pi^*_{CO}/\sigma_{C\text{-}Het}$ and π^*_{CO}/n_O orbital interactions are the main factors that stabilize their *gauche* rotamers in the ground state. Our investigations on some *p*-substituted α-phenylthioacetones[3] by IR spectroscopy have indicated a small sensitivity of the ν_{CO} (*cis*) frequencies on going from electron-attracting to electron-donating substituents, due to the Field and Inductive Effects, which act in opposition in the *cis* rotamer, practically cancelling each other. Moreover the decreasing *cis/gauche* population ratio on going from electron-attracting to electron-donating substituents have suggested the occurence of the $\pi^*_{CO}/\sigma_{C\text{-}S}$ hyperconjugative interaction in the *gauche* rotamers of the title compounds.

As an extension of these previous studies, the present paper deals with IR and ^{13}C NMR investigations of some *p*-substituted α-phenoxyacetones X-PhO-CH_2-C(O)Me, bearing at *para* position electron-attracting, hydrogen and electron-donating substituents.

The main scope of this work was to verify in what extent the increased ionization energy of the oxygen lone pair (n_O) and the $\sigma_{C\text{-}O}$ orbital ($-CH_2-\ddot{O}$ bond) in relation to the sulfur lone pair (n_S) and the $\sigma_{C\text{-}S}$ orbital ($-CH_2-\ddot{S}$ bond in α-arylthioacetones),[3] affect the Coulombic and electronic interactions in the *cis* and *gauche* rotamers and consequently their stabilities in the α-aryloxyacetones series.

The *equatorial-axial* conformational equilibrium studies of some *p*-substituted α-phenoxycyclohexanones by ^1H NMR spectroscopy,[4] showed that in carbon tetrachloride, there is a linear correlation between the *equatorial/axial* relative concentrations and the σ_p parameter, when the *para* substituent changes from hydrogen to electron-attracting substituents. However, in acetonitrile, the *equatorial/axial* ratio was constant for the whole series.

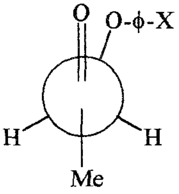
More recently, dipole moments and molar Kerr constants for some *p*-substituted α-phenoxycyclohexanones, as well as for α-phenoxy- and α-(*p*-nitrophenoxy)-acetones have been determined.[5] An increase of the concentration of the *syn*-periplanar (*equatorial* form) in relation to the *anti*-clinal (*axial* form) with the increase of the polar character of the *para*-substituent was observed. Their *cis/gauche* isomerism was also detected by IR spectroscopy.

However, all the above cited papers do not give effective explanations on the nature of the stability of *equatorial-axial* and of *cis-gauche* conformers for the studied compounds.

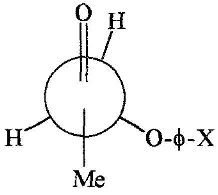
RESULTS AND DISCUSSION

Stretching frequencies and absorbance ratios of the analytically resolved carbonyl doublets for the *p*-substituted α-phenoxyacetones (**1-6**) in carbon tetrachloride (fundamental and 1st overtone), in chloroform and in acetonitrile are given in Table 1. Frequencies of parent acetone **7** are included for comparison.

The absorbance ratio between higher and lower frequency components for all compounds (**1-6**), increases progressively from carbon tetrachloride to chloroform, and then to acetonitrile solutions, as the solvent polarity increases. Fig.1 illustrates the solvent effects on the doublet components of compound **3**. These solvent effects and the occurrence of two carbonyl bands in the 1st overtone region at frequencies, *ca.* twice those of the fundamental, and with nearly the same intensity ratios, strongly indicate that compounds **1-6** display a *cis-gauche* rotational isomerism.[7,8] Thus, it may be assumed[1] that higher frequency bands corresponds to more polar (*cis*) conformer (I) while lower frequency bands belongs to less polar (*gauche*) conformer (II).



(I)



(II)

It should be noticed that there is a progressive decrease of the ν_{CO} frequencies of the *gauche* conformers for the phenoxyacetones **1-6** (Table 1), in all solvents, on going from electron-attracting to electron-donating *para* substituents (eg. $\nu_{CO} = 3.67\sigma_p + 1726.0$; r=0.991; in CCl_4;

TABLE 1. Frequencies and intensity ratios of carbonyl stretching bands in IR spectra of *p*-substituted α-phenoxyacetones X-ϕ-$OCH_2C(O)Me$ (**1**-**6**) and frequencies of acetone **7**.

		CCl_4				$CHCl_3$		CH_3CN	
Cpd.	X	ν[a]	α_c/α_g[b]	ν[c]	α_c/α_g	ν	α_c/α_g	ν	α_c/α_g
1	NO_2	1747.2	0.46	3473.5	0.46	1741.3	0.89	1738.6	3.68
		1728.9		3438.8		1723.9		1724.2	
2	Br	1746.9	0.23	3472.5	0.28	1740.0	0.59	1738.0	2.36
		1727.3		3435.1		1721.7		1723.4	
3	Cl	1746.0	0.24	3472.6	0.27	1739.9	0.63	1738.0	2.53
		1726.9		3434.8		1721.7		1723.3	
4	H	1747.0	0.18	3473.7	0.20	1741.0	0.42	1737.4	1.61
		1726.1		3433.7		1720.8		1722.9	
5	Me	1746.0	0.17	3472.8	0.17	1739.1	0.59	1737.9	1.86
		1725.4		3432.2		1719.5		1722.1	
6	OMe	1744.8	0.17	3471.6	0.20	1738.5	0.55	1737.7	1.45
		1724.9		3431.4		1719.4		1721.9	
7	–[d]	1718.5	–	3418.0	–	1711.5	–	1714.5	

[a]In cm^{-1}; [b]Absorbance ratios for the higher and the lower frequency components of the analytically resolved carbonyl band; [c]1st overtone; [d]Acetone, from ref. 6.

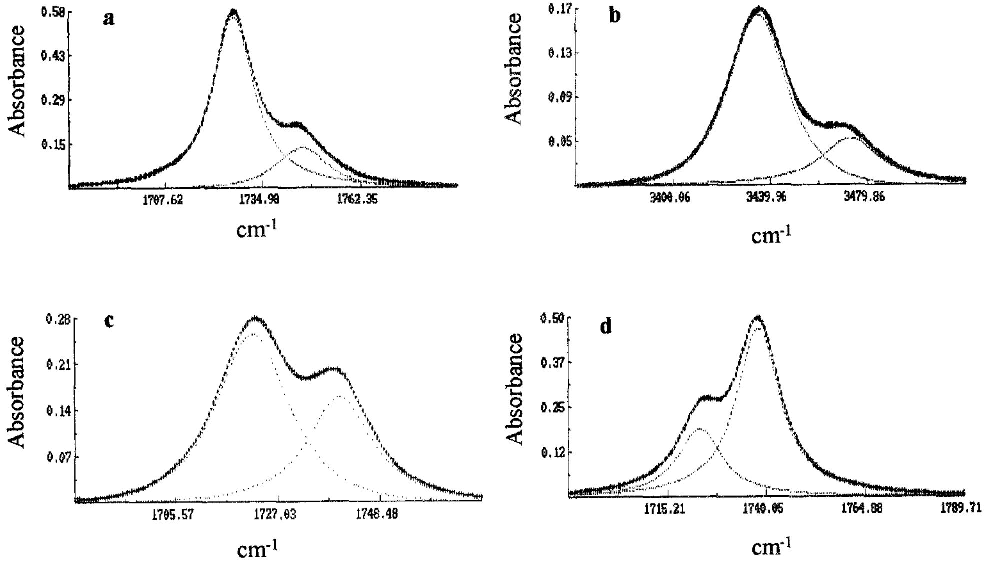


FIG.1 - I.R. Spectra of a-(*p*-chlorophenoxy)-acetone **3** showing the analytically resolved carbonyl stretching bands, in carbon tetrachloride [fundamental (a) and 1st *overtone* (b)], *chloroform* (c) and acetonitrile (d).

σ_p from ref. 9). In the case of *cis* conformers only small changes in the ν_{CO} frequencies occur. The carbonyl frequency shifts (Δν) for *cis* and *gauche* rotamers of compounds **1-6** expressed in relation to the parent compound **7**, in carbon tetracloride (Table 2) illustrate well this behavior.

It should be pointed out that the significant positive carbonyl *cis* shifts (mean value of 27.8 cm^{-1}) are in agreement with the summing up of the Repulsive Field Effect (F), between the C=O and C-O dipoles and the -I Inductive Effect of the aryloxy substituent.[1] On the other hand, the less positive shifts (mean value of +8.1 cm^{-1}) for the *gauche* rotamers, may be ascribed to occurrence of the π^*_{CO}/n_O and π^*_{CO}/σ_{C-O} orbital interactions[1] that act in opposition to -I effect of the α-aryloxy substituent.

A nearly constant increase of *cis*/*gauche* ratio (ca. 9x) for compounds **1-6** (Table 1), going from non polar (carbon tetrachloride) to polar solvent (acetonitrile), irrespective to the nature of the *para* substituent of the aryloxyl group was observed.

Table 1 also shows there is a progressive decrease of the *cis*/*gauche* population ratio, for compounds **1-6**, on going from electron-attracting to electron-donor *para* substituents (eg. $\alpha_c/\alpha_g = 2.05\sigma_p + 1.94$; r = 0.972; in CH_3CN), in all solvents.

Both, the changes of the *cis*/*gauche* ratios and the small sensitivity of the $\nu_{CO(cis)}$ frequencies may be explained through analysis of two extreme cases of *cis* conformers as follows:(Structures III and IV, Fig. 2).

For a strong electron-attracting substituent, such as nitro group in *para* position of a phenoxyacetone, there will be a direct conjugation between the oxygen lone pair and the *p*-nitrophenyl group, resulting in a smaller negative charge at the α-oxygen atom (Structure IV, Fig. 2), in comparison to the corresponding oxygen atom in the parent

TABLE 2. Carbonyl frequency shifts[a,b] for *cis* ($\Delta\nu_c$) and *gauche* ($\Delta\nu_g$) rotamers of *p*-substituted α-phenoxyacetones X-ϕ-$OCH_2C(O)Me$ **1-6**, (CCl_4).

Compd.	X	$\Delta\nu_c$	$\Delta\nu_g$
1	NO_2	+28.7	+10.4
2	Br	+28.4	+8.8
3	Cl	+27.6	+8.4
4	H	+28.5	+7.6
5	Me	+27.5	+6.9
6	OMe	+26.3	+6.4

[a] $\Delta\nu_c$ and $\Delta\nu_g$ refers to the difference: ν[X-ϕ-$OCH_2C(O)Me$] - ν[$Me_2C(O)$], for the *cis*- and *gauche*-rotamers, respectively; [b] In cm^{-1}.

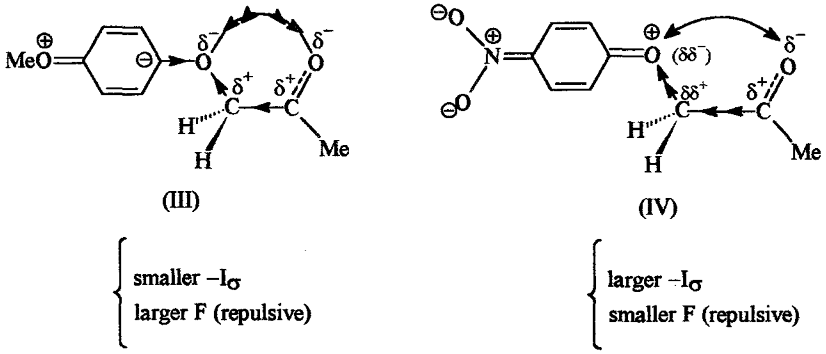


FIG.2 - *Cis* conformers of α-(*p*-methoxyphenoxy)- (III) and α-(*p*-nitrophenoxy)acetone (IV) showing Field (F) and Inductive Effects (-I).

α-phenoxyacetone. This conjugation originates a stronger $-I_\sigma$ inductive effect[10] ($\sigma_{I(O2N\text{-}PhO\text{-})} = 0.47$),[11] which is transmitted through the bonds, leading to an increased double bond character of the carbonyl group. On the other hand, the smaller negative charge at the α-oxygen atom of the p-nitrophenoxyl group will induce through space a smaller repulsive Field Effect (F) between this α-oxygen and the carbonyl oxygen atom, leading to a decrease in the carbonyl double bond character. Thus, this practically cancels out the increased inductive effect $-I_\sigma$ of the *p*-nitrophenoxyl group, in comparison with the unsubstituted phenoxyl group ($\sigma_{I(PhO\text{-})} = 0.42$)[11] of the parent α-phenoxyacetone.

In the opposite case, when there is a strong electron-donating substituent, such as a methoxy group, in the *para* position, an increased negative charge at the oxygen atom of the *p*-methoxyphenoxyl group (Structure III, Fig.2) will occur, in comparison with that of the phenoxyl group of the parent phenoxyacetone. This will originate a smaller $-I_\sigma$ inductive effect of the *p*-methoxyphenoxyl group ($\sigma_{I(MeO\text{-}PhO\text{-})} = 0.39$)[11] 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. Thus, the interaction between the α-oxygen of the *p*-methoxyphenoxyl group and the carbonyl oxygen atoms leads to a stronger repulsive Field Effect[9] (F), and as a consequence, to an increase in the double bond character almost cancelling out the decreased $-I_\sigma$ inductive effect, in comparison with the unsubstituted phenoxyl group. So, the almost invariability of the carbonyl double bond character in the two analyzed extremes should be responsible for the small changes in carbonyl force constants and, consequently, in ν_{CO} frequencies, for the *cis* rotamers in the whole series. Moreover, this qualitative analysis also suggests that the *cis* rotamer should have almost the same energy for all of the title compounds.

The decrease in *cis*/*gauche* population ratios of **1**-**6**, in all solvents (Table 1), can be mainly ascribed to an increasing stabilization of the *gauche* rotamers. The nature of the stabilization of the *gauche* rotamers may be discussed as outlined below.

The ionization energy of the unperturbed oxygen lone pair orbital in phenoxymethane (11.02 eV)[12] is significantly closer to the unperturbed π^*_{CO} orbital in acetone (attachment energy 1.26 eV),[13] while the ionization energy of the unperturbed $\sigma_{C\text{-}O}$ orbital in phenoxymethane (> 15 eV)[12] is far apart from the unperturbed π^*_{CO} orbital. Therefore, in the *gauche* rotamers, a strong π^*_{CO}/n_O interaction should occur in comparison with the weak $\pi^*_{CO}/\sigma_{C\text{-}O}$ hyperconjugative interaction (Fig.3).

The ionization energy of the oxygen lone pair in *p*-methoxyanisole (10.25 eV) is significantly smaller than that of *p*-nitroanisole (11.75 eV).[12] Therefore, the π^*_{CO}/n_O orbital interaction should be stronger in the *p*-methoxy-derivative **6**, in comparison with the *para*-nitro-derivative **1**, for which the unperturbed π^*_{CO} and the n_O orbital energy levels are far apart. This trend leads to a stronger stabilization of the *gauche* rotamer of compound **6** in relation to compound **1**. The increased electrostatic attraction between the negatively charged α-oxygen atom of the *p*-methoxy-phenoxyl group and the positively charged carbonyl carbon in the *gauche* rotamer of **6** should stabilize this rotamer to a larger extent, in comparison to the *gauche* rotamer of **1**, with weaker electrostatic attraction between the less negatively charged α-oxygen atom of the *p*-nitrophenoxyl group and the less positively charged carbonyl carbon (Structures V and VI, Fig. 4).

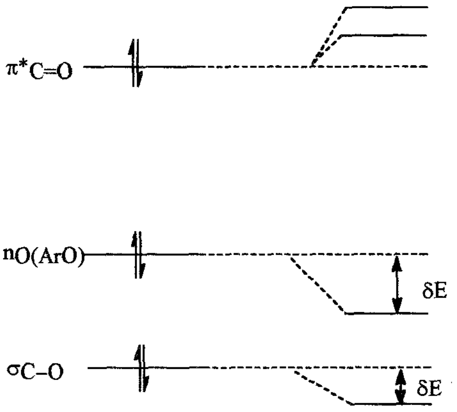


FIG.3 - Qualitative energy level diagram showing the strong π^*_{CO}/n_O and weak $\pi^*_{CO}/\sigma_{C\text{-}O}$ orbital interactions in *gauche* rotamers of **1-6**.

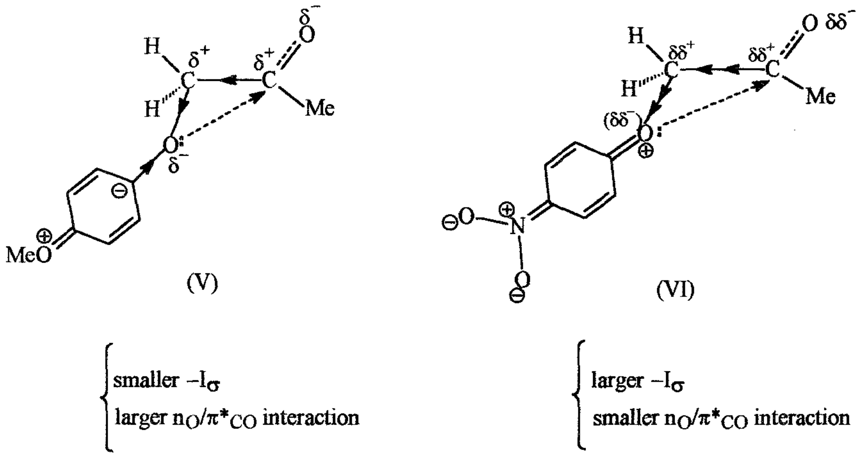


FIG.4 - Stabilization of *gauche* rotamers by electrostatic and $n_O \rightarrow \pi^*_{CO}$ orbital interactions for α-(*p*-methoxyphenoxy)- (V) and α-(*p*-nitrophenoxy)-acetone (VI).

These trends make clear that both the π^*_{CO}/n_O interaction and the attractive Coulombic interaction (between $Ar^{\delta+}-O^{\delta-}$ and $C^{\delta+}=O^{\delta-}$ dipoles) should be responsible for the progressive stabilization of the *gauche* rotamer of **1**-**6**, on going from electron-attracting to electron-donating substituents.

Furthermore, the above mentioned interactions should also be responsible for the progressive decrease of the carbonyl force constants and thus in their frequencies (Table 1) and in the *gauche* rotamers carbonyl frequency shifts (Table 2).

^{13}C NMR data show that a progressive shielding effect for the carbonyl (3.0 ppm) and α-methylene (0.9 ppm) carbons, on going from electron-donating (OMe) to electron-attracting (NO_2) *para*-substituents, for **1**-**6**, is observed (Table 3).

Since IR analysis showed that the *cis* rotamers have almost the same carbonyl bond order in the whole series, it may be inferred that practically the same shielding of *cis* rotamers carbonyl carbon should be expected.

The smaller polarization of the carbonyl double bond for the *gauche* rotamer of the *p*-nitro-derivative **1** (Structure VI, Fig. 4), should originate a larger shielding at the carbonyl carbon, in relation to the *gauche* rotamer of the *p*-methoxy-derivative **6**, where a larger polarization of the carbonyl double bond shall occur. This is in line with the observed shielding trends at the carbonyl carbon of **1**-**6** (Table 3).

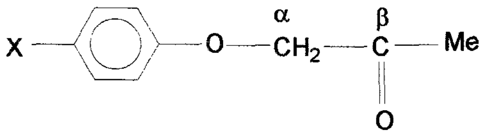
As a weaker π^*_{CO}/n_O orbital interaction in the *gauche* rotamer of **1** in relation to the stronger π^*_{CO}/n_O interaction in the *gauche* rotamer **6** shall occur, a lower shielding effect at the carbonyl carbon of compound **1** than in **6** should be expected, in opposition to the data of Table 3. Thus, it may be concluded that the Inductive (-I) and Field (F) Effects should prevail over the π^*_{CO}/n_O orbital interaction. Moreover, the increasing shielding

TABLE 3. ^{13}C NMR chemical shifts[a] for the carbonyl and α-methylene carbons of *p*-substituted α-phenoxy-acetones, X-ϕ-OCH$_2$C(O)Me, in CDCl$_3$.

Compound	X	δ_{CO}	δ_{CH2}
1	NO$_2$	203.10	72.92
2	Br	204.61	72.87
3	Cl	204.21	72.54
4	H	205.13	72.48
5	Me	205.64	72.77
6	OMe	206.11	73.75

[a] In ppm relative to TMS.

effect of the carbonyl carbon (in β-position to aryloxyl group; VII), on going from electron-donating to electron-attracting groups, is larger than that of the methylene carbon (in α-position; VII). This trend shows an opposite behavior to what has been observed in our previous work,[3] which dealt with ^{13}C NMR study of X-ϕ-S-CH$_2$-Y (Y:C=O, C≡N and CH$_3$).



(VII)

This anomalous variation of the shielding effects, in the α-phenoxy-acetones series, seems to indicate that the attractive Field Effect between the Ar$^{\delta+}$–O$^{\delta-}$ and C$^{\delta+}$=O$^{\delta-}$ dipoles, prevails over the -I$_\sigma$ effect and consequently over the π^*_{CO}/n_O orbital interaction. Finally the ^{13}C NMR data show that the stabilization of the *gauche* rotamers is mainly determined by the attractive Field Effect between the $Ar^{\delta+}-O^{\delta-}$ and $C^{\delta+}=O^{\delta-}$ dipoles and in minor extent by the π^*_{CO}/n_O orbital interaction.

EXPERIMENTAL

Materials - All solvents for spectrometric measurements were spectrograde and were used without further purification. Commercial acetone was purified as described elsewhere.[14] The following *p*-substituted α-phenoxyacetones: nitro[15] (**1**), chloro[16] (**2**), bromo[15] (**3**), hydrogen[17] (**4**), methyl[15] (**5**) and methoxy[18] (**6**) already described in the literature, were prepared essentially by the method of Hurd and Perletz[17] described for **1**. They were analyzed by g.l.c. to assess their purity.

IR Measurements - The IR spectra were obtained with a Nicolet FT-IR Magna 550 spectrometer, with 1.0 cm^{-1} resolution. The carbonyl stretching region (1850-1600 cm^{-1}) was recorded in 2.0×10^{-2} $mol.dm^{-3}$ carbon tetrachloride, chloroform, and acetonitrile solutions, using a 0.519 mm NaCl cell. The carbonyl first overtone region (3600-3100 cm^{-1}) spectra were obtained in 2.0×10^{-2} $mol.dm^{-3}$ in carbon tetrachloride solutions using 1.00 cm quartz cell. The overlapped carbonyl stretching bands were computationally deconvoluted as previously described.[19] The *cis*/*gauche* relative concentrations were estimated from the absorbance ratio at the maxima (α_c/α_g) of the carbonyl band components, assuming equal molar absorptivity coefficients for both rotamers.

NMR measurements - The conditions for recording ^{13}C NMR spectra have been described elsewhere.[19]

Acknowledgments

The authors thank the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for financial support and the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for scholarships (to M.L.T. Hui, S.Harms and M.S.V. Schimidt) and for a grant (to P.R.O. and R.R.).

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Date Received: April 16, 1999
Date Accepted: August 1, 1999