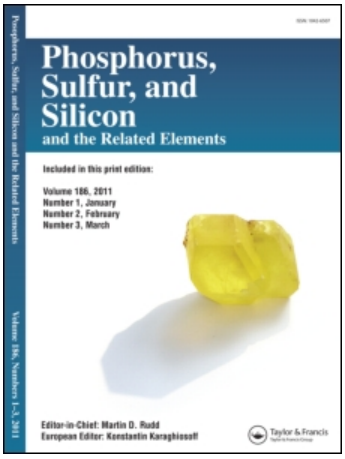

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CONFORMATIONAL AND ELECTRONIC INTERACTION STUDIES OF SOME (ALKYLTHIO)-SUBSTITUTED PROPANONES AND THEIR MONO- AND DI-OXIDATED DERIVATIVES.

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ABSTRACT The analysis of the carbonyl frequency shifts hyperconjugative parameters ($\Delta\nu_H$) along with the Non-Additivity Effect of the α-methylene carbon chemical shifts for the ethylthio- (1), ethylsulfinyl- (2) and ethylsulfonyl- (3) propanones indicated the occurrence of both $\pi^*_{CO}/\sigma_{C-SO_n}$ and $\pi_{CO}/\sigma^*_{C-SO_n}$ interaction in the ground state of their gauche conformers. The bathochromicaly shifted $n \rightarrow \pi^*_{CO}$ transition of the title compounds in relation to the parent compound indicated the existence of the $\pi^*_{CO}/\sigma^*_{C-SO_n}$ interaction in the excited state of their gauche rotamers.

INTRODUCTION

Our previous studies of some ω-(ethylthio)-acetophenones[1] and their mono- and di-oxidated derivatives[2] have suggested the existence of the $\pi^*_{CO}/\sigma_{C-SO_n}$ and $\pi_{CO}/\sigma^*_{C-SO_n}$ orbital interactions in the ground state of their gauche rotamers.

Aiming to improve our knowledge on the mentioned interactions we have recently studied[3] the (alkylthio)-, (alkylsulfinyl) and (alkylsulfonyl)-propanones by I.R., ^{13}C NMR and U.V. spectroscopies helped by Molecular Mechanics Calculations. However, the present communication deals only with the ethyl- derivatives taken as representative compounds of the whole series.

RESULTS AND DISCUSSION

Table 1 shows the carbonyl stretching frequencies and the frequency shifts for the most stable rotamer which is a gauche one of the (ethylthio)- (1), (ethylsulfinyl)- (2), and (ethylsulfonyl)- (3) propanones whose average popula-

tion for the whole serie is ca. 70% along with the datum of the 2-pentanone (4), taken as the reference compound. This Table also includes the inductive parameters (σ_I) of the substituents and the computed carbonyl frequency shifts ($\Delta\nu_H$) induced by the hyperconjugative effect of the substituents.

TABLE I Carbonyl stretching frequencies[a] and the frequency shifts ($\Delta\nu_g$)[b] for the most stable gauche rotamer of ethylthio-, ethylsulfinyl- and ethylsulfonyl-propanones $MeC(O)CH_2X$, in CCl_4; inductive parameters (σ_I)[c] and computed carbonyl frequency shifts induced by the hyperconjugative ($\Delta\nu_H$)[d] effect of the substituents.

Compd.	X	ν	$\Delta\nu_g$	σ_I	$\Delta\nu_H$
(1)	SEt	1711	-9	0.25	-14.9
(2)	SOEt	1715	-5	0.50	-16.8
(3)	SO_2Et	1721	+1	0.60	-13.1
(4)	Et[d]	1720	-	-	-

[a] In cm^{-1}; [b] $\Delta\nu_g$ refers to the difference: ν(substituted propanone) - ν(parent compound); [c] From ref. 5; [d] From ref. 4.

It is worthy of noting that instead of the expected rising in the carbonyl frequency due to the electron--attracting inductive effect of the α-thiosubstituents, their gauche shifts vary from negative to nearly zero values with the increasing degree of oxidation of the sulfur atom.

As previously proposed[4] for the α-heterosubstituted acetones this abnormal behavior suggests the occurrence of the hyperconjugative interaction between the π^*_{CO} and σ_{C-X} orbitals, acting in opposition to the inductive effect of the α-substituents, originating a lowering of the carbonyl frequencies of the α-thiosubstituted derivatives (1)-(3) in relation to the parent compound (4).

It should be pointed out that the computation of the carbonyl frequency shifts induced by the hyperconjugative effect of the substituents has already been reported for the heterosubstituted acetones[4]. Table 1 shows that $\Delta\nu_H$ of the thiosubstituents are negative and follow in absolute value the order: ethylsulfinyl > ethylthio > ethylsulfonyl.

Table 2 shows the experimental and the calculated α-methylene carbon chemical shifts, in chloroform, for the

thiosubstituted propanones (1)-(3) and iodopropanone (5) as well as the difference between them i.e. the Non-Additivity effects (NAE).

TABLE II ^{13}C NMR Chemical shifts[a] and the Non-Additivity effects ($\Delta\delta$)[b] for the methylene carbon of the substituted propanones $MeC(O)-CH_2-X$, in $CDCl_3$

Compd.	X	δ_{CH_2}	$\Delta\delta$
(1)	SEt	41.5 49.9[c]	-7.5
(2)	SOEt	62.2 69.5	-7.3
(3)	SO_2Et	62.9 70.7	-7.8
(5)	I[d]	6.0 17.6	-11.6

[a] In ppm; [b] $\Delta\delta = \delta_{exp.} - \delta_{calc.}$; [c] Calculated value; [d] From ref. 6.

According to Nesmeyanov[7] the additional shielding on the α-methylene carbon may be ascribed to an increase in the double bond character between the α-methylene carbon and the carbonyl group due to the π^*_{CO}/σ_{C-X} hyperconjugative interaction. However, in spite of the $\Delta\nu_H$ mean value for the sulfurated substituents (1)-(3) being very close to the value of the iodo substituent (5) i.e. -15 cm^{-1} and -16 cm^{-1} respectively, the NAE mean value of the α-methylene carbon for the sulfurated propanones -7.5 ppm is almost half the value of the iodopropanone (-11.6 ppm).

Consequently, the $\Delta\nu_H$ values for the α-sulfurated substituents superestimate the hyperconjugative contribution. Therefore as suggested before[1,2] these values should result from the simultaneous occurrence of the $\pi^*_{CO}/\sigma_{C-SO_n}$ and $\pi_{CO}/\sigma^*_{C-SO_n}$ orbital interactions. This proposition can be better evidenced in the light of the M.O. Perturbation Theory[8] as follows.

As is well know δE is a measure of the orbital interaction and it is given by the equation: $\delta E = \frac{(H_{\sigma\pi})^2}{\Delta E}$.

Assuming that $H_{\sigma\pi}$ is constant and equal to 1 for both $\pi^*_{CO}/\sigma_{C-SO_n}$ and $\pi_{CO}/\sigma^*_{C-SO_n}$ orbital interactions, thus

their corresponding δE and $\delta E'$ values can be computed for the whole thiosubstituted propanones series.

Considering that for the $\pi^*_{CO}/\sigma_{C-SO_n}$ interaction the energy difference ΔE between π^*_{CO} (A.E.† 1.3 eV for 2-pentanone) and σ_{C-SO_n} unperturbed orbitals decreases progressively from n= 2 (I.E.† for dimethylsulfone is 14.0 eV), to n= 1 (I.E. for dimethylsulfoxide is 13.4 eV) and to n= 0 (I.E. for the dimethylsulfide is 12.7 eV), δE will be greater for the orbital interaction between π^*_{CO} and σ_{C-S} (δE_1= 0.071 eV), lower with σ_{C-SO} (δE_2= 0.068 eV) and still lower with σ_{C-SO_2} (δE_3= 0.065 eV).

Therefore, the $\pi^*_{CO}/\sigma_{C-SO_n}$ hyperconjugative interaction is more important for the keto-sulfides and becomes progressively less significant for the keto-sulfoxides and keto-sulfones.

As for the $\pi_{CO}/\sigma^*_{C-SO_n}$ orbital interaction a different behavior may be noticed due to the fact that the A.E. data of the $\sigma^*_{C-SO_n}$ unperturbed orbitals of the dimethylsulfide (3.25 eV), dimethyl sulfone (3.15 eV) and dimethyl sulfoxide (2.30 eV) follow an unexpected order in relation to the unperturbed π_{CO} orbital of the 2-pentanone (I.E.= 11.7 eV). Thus, in this case a larger interaction ($\delta E'$) shall occur between π_{CO}/σ^*_{C-SO} orbitals ($\delta E'_2$= 0.071 eV) than that between $\pi_{CO}/\sigma^*_{C-SO_2}$ and π_{CO}/σ^*_{C-S} orbitals, whose $\delta E'_3$ and $\delta E'_1$ values are very close i.e. 0.067 eV and 0.066 eV, respectively.

It can be seen in Figure 1 that the order of the summing up of the δE and $\delta E'$ values is the same as that of the hyperconjugative parameter of the substituents ($\Delta\nu_H$) i.e. SOEt > SEt > SO_2Et. Consequently, these results strongly support our proposition that the $\Delta\nu_H$ parameter for the alkylthio-, alkylsulfinyl- and alkylsulfonyl substituents depends on the simultaneous contribution of the $\pi^*_{CO}/\sigma_{C-SO_n}$ and $\pi_{CO}/\sigma^*_{C-SO_n}$ interactions.

Table 3 shows the U.V. data of the ethylthio-propanone (1) and their corresponding mono- (2) and di-oxidated derivatives in ethanol. In this Table a batho- and hyperchromic effect of the $n \rightarrow \pi^*_{CO}$ transition of the title compounds in relation to the propanone (6) is observed.

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† A.E. and I.E. refers to the attachment and ionization energy respectively.

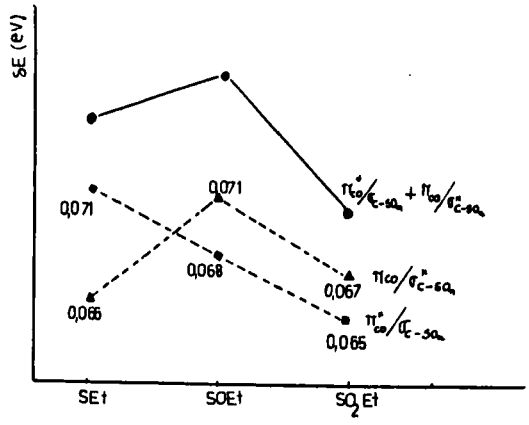

FIGURE 1 Qualitative energy diagram showing the relative contributions of $\pi^*_{CO}/\sigma_{C-SO_n}$ (δE) (■) and $\pi_{CO}/\sigma^*_{C-SO_n}$ (δE') (▲) orbital interactions in thiosubstituted propanones.

TABLE III U.V. data for the carbonyl n → π* transition of the substituted propanones $MeC(O)CH_2X$, in ethanol.

X	Compd.	λ[a]	ε[b]
SEt	(1)	295	308
SOEt	(2)	287	70
SO_2Et	(3)	286	65
H[c]	(6)	278	18

[a] In nm; [b] Apparent molar absorptivity in $l.mol^{-1}.cm^{-1}$; [c] Parent compound.

The bathochromic effect may be ascribed to an interplay of the hyperconjugative interaction between the $\sigma^*_{C-SO_n}$ and π^*_{CO} orbitals and the inductive effect of the α-thiosubstituents.

The stabilization of the carbonyl lone pair $n_{O(CO)}$ should occur in larger extent than that of π^*_{CO} orbital, before the orbital interaction, due to the electron-attracting effect of the α-thiosubstituents (Table 1). Therefore after the hyperconjugative interaction between the inductively stabilized π^*_{CO} and $\sigma^*_{C-SO_n}$ orbitals a larger stabilization of the π^*_{CO} orbital shall occur in

relation to the carbonyl oxygen lone pair originating a lowering in the energy of the $n \rightarrow \pi^*_{CO}$ transition for the title compounds in relation to the parent compound.

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