Photoelectron Spectroscopy and *Ab-initio* Study of the Conformation of ω-Ethylthioacetophenones

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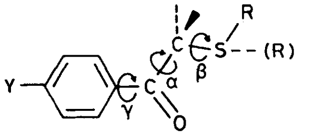
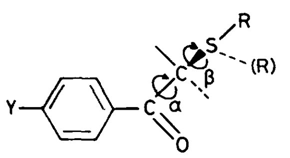
The He^I photoelectron spectra of ω-ethylthioacetophenones $Y\text{-}C_6H_4COCH_2SC_2H_5$ (Y = NO_2, CN, H, Me, OMe) are assigned by means of the composite-molecule approach and *ab-initio* pseudopotential computations. The splitting of the first band—deriving from sulphur lone-pair ionization—observed when Y is an electron-withdrawing substituent is ascribed to the presence of two groups of rotamers. On experimental basis it is concluded that, in the most abundant conformer, the sulphur lone pair is nearly parallel to the π-system, while it is stabilized by distortion from planarity and $S \longrightarrow \pi^*$ charge-transfer interaction in the other conformer. Theoretical results on conformational stability (while obtained by means of a quite crude approach) are in agreement with this interpretation.

We have recently reported[1] a He^I and He^{II} u.v. photoelectron (p.e.) spectroscopy and theoretical study of *para*-substituted ω-halogenoacetophenones. Our *ab-initio* minimal basis set calculations using the pseudo-potential method[2,3] indicated, in agreement with i.r. solution data,[4] that in the most stable conformation the carbon–halogen bond prefers a *gauche* orientation with respect to the C=O bond. The p.e. spectral data confirmed this conclusion. In addition, the first band in the spectra of the iodine derivatives showed, with respect to the corresponding acetophenones, peculiar energy and intensity variations on changing the *para*-substituent. These findings were ascribed, in addition to a hyperconjugative interaction between the highest occupied MO (HOMO) and the σ (C–I) MO, to a through-space mixing of the halogen lone pairs with the π-MOs localized at the CO group owing to their low ionization energy (IE) value and large size.[1]

Since the sulphur lone-pair orbitals in principle possess similar characteristics to the halogen lone pairs, we have undertaken the corresponding p.e. spectral and theoretical analysis of the *para*-substituted ω-ethylthioacetophenones (**1**)—(**5**), the results for which are presented in this paper.



γ = 0°, α = 0°, β = 0°, (90°)



α = 90°, β = 0°, (90°)

(**1**) Y = NO_2; (**2**) Y = CN; (**3**) Y = H; (**4**) Y = Me; (**5**) Y = OMe

Previous i.r. and u.v. spectra of compounds (**1**)—(**5**) were interpreted[5] as being due to a mixture of *cis* (*ca.* 10%) and *gauche* (*ca.* 90%) rotamers. In the latter, the π(CO)—σ(C–S) hyperconjugation was considered responsible for the progressive decrease, with respect to the corresponding acetophenones, of the carbonyl stretching frequency on going from electron-donating to electron-accepting *para*-substituents. Similarly, the bathochromic shift and the hyperchromic effect of the $\pi^* \longleftarrow n$ transitions were interpreted as deriving from hyperconjugative interaction between the π*(CO) and σ*(C–S) orbitals. The ^{13}C n.m.r. data, however, were not in accordance with the above model, the shifts of the methylene carbon being in the opposite direction to that expected if hyperconjugation were the predominant effect.

Experimental

The He^I photoelectron spectra were recorded using a Perkin-Elmer PS 18 photoelectron spectrometer and calibrated with noble gas lines. The error in the quoted IE values is ±0.05 eV where two decimal places are given and ±0.1 eV in other cases.

The ω-ethylthioacetophenones (**1**)—(**5**) were prepared as previously described.[5]

Ab-initio LCAO-MO-SCF computations using the non-empirical pseudo-potential method of Bartelat *et al.*[2] gave satisfactory results with ω-halogenoacetophenones.[1] For this reason, the same method has been used to compute the localization properties of the valence MOs, their energy shifts with geometrical parameters, and the preferential conformation of compounds (**1**) and (**3**). All calculations were carried out using the PSHONDO program[3] which includes pseudo-potentials. To reduce the computational effort in view of the relative large size of the compounds studied, a hydrogen atom was substituted for the ethyl group and the computations were performed using the minimal basis set apart from the inclusion of the polarization functions on sulphur. Standard bond length and bond angle values were used. Considering that hyperconjugative interactions were proposed to rationalize the i.r. and u.v. data,[5] optimization of the C–SH bond distance (*r*) and of the C–Ĉ–S bond angle could appear important. However, we have recently optimized[6] the C–Ŝ–C bond angle, α, and the C–S bond distances in some *para*-substituted α-phenylthioacetonitriles (**6**) at β values

(**6**)

Table 1. *Ab-initio* pseudo-potential theoretical results on conformational preferences of *para*-substituted ω-mercaptoacetophenones, YC_6H_4-$COCH_2SH$, relative energies in kJ mol^{-1}

Torsion angles (°)	α = 0°		α = 90°		
			Y = H		
β	Y = H	Y = NO_2	*a*	*b*	Y = NO_2
0	0	0	3.68	5.44	2.89
45	8.22	7.84	7.06	8.45	6.38
90	9.08	8.42	1.68	3.01	0.63
135	2.52	2.36	1.97	0	1.03
180	*c*	*c*	4.60	4.74	4.39
225	2.52[d]	2.36[d]	0	1.80	0
270	9.08[d]	8.42[d]	1.71	3.40	1.08
315	8.22[d]	7.84[d]	4.97	6.36	3.91

[a] r_{C-S} = 1.82 Å. [b] r_{C-S} = 1.83 Å. [c] These values have not been computed because the substitution of a hydrogen atom for an ethyl group adopted in our calculations could give unrealistic results due to different stereoelectronic interactions with respect to the real molecules. [d] The total energy values for β 225, 270, and 315° correspond to those of the rotamers with β 135, 90, and 45°, respectively, because of the symmetry of the planar (α, 0, γ 0°) molecular skeleton with respect to the variation of β in both directions.

ranging from 0—90°. The variations of *r* and α for a given β were ⩽0.009 Å and ⩽7.1°, respectively. In addition, the values of these parameters have a small effect (⩽ 1 kcal mol^{-1} for Y = NO_2 and H) on the total energy.[6] To ascertain that also in the present molecules these parameters have no large effects on the total energy, some data have been checked taking $r' = r + 0.01$ Å. The torsional angles were varied as described below.

Because of this crude approach, the conformational results are considered to provide only qualitative information.

Results

Theoretical Calculations.—The theoretical results on orbital energies and composition and their conformational dependence will be discussed in the next section together with the spectra. In this section we present the effects of the variation of geometrical parameters on the total energy.

The p.e. spectra of ω-ethylthioacetophenones (**1**) and (**2**) bearing an electron-withdrawing *para*-substituent show a broadening of the first band (see below) ascribed to the presence of a distribution of rotamers with different HOMO energy. This effect is not shown by the remaining derivatives where Y is H or an electron-releasing group. Total energy calculations of compounds (**1**) and (**3**), representative of two different electronic situations, were performed to mimic the influence of the Y substituent on the conformational stabilities.

Of the three torsional angles, α, β, and γ, the last was not varied because it is well established[1,7–16] that in acetophenone, its *para*-substituted derivatives, and their ω-derivatives, the C–O bond lies in the plane of the benzene ring (γ 0°) in the solid, solution, and gas phase. As far as the torsional angle α is concerned, calculations have been performed at 0 and 90°, in accordance with the solution i.r. data.[5]

Relative energies (kJ mol^{-1}) of conformers of compounds (**1**) and (**3**) at selected α and β values are reported in Table 1. The two compounds exhibit very similar behaviour. For α 0°, the most stable conformer has β 0°, while the energy maximum occurs for β 90°. The potential energy curve for α 90° shows, for both compounds, three minima at about 0, 90, and 225°. To verify the reliability of these results, the potential energy curve for *x* = H and α 90° has been recomputed at a C–SH bond distance longer than the standard value by 0.01 Å (the maximum Δ*r* previously observed[6] in the optimization of C–S bond distances in closely related compounds, see above). Table 1 indicates that the energy trend is nearly parallel to that computed at the standard bond distance.

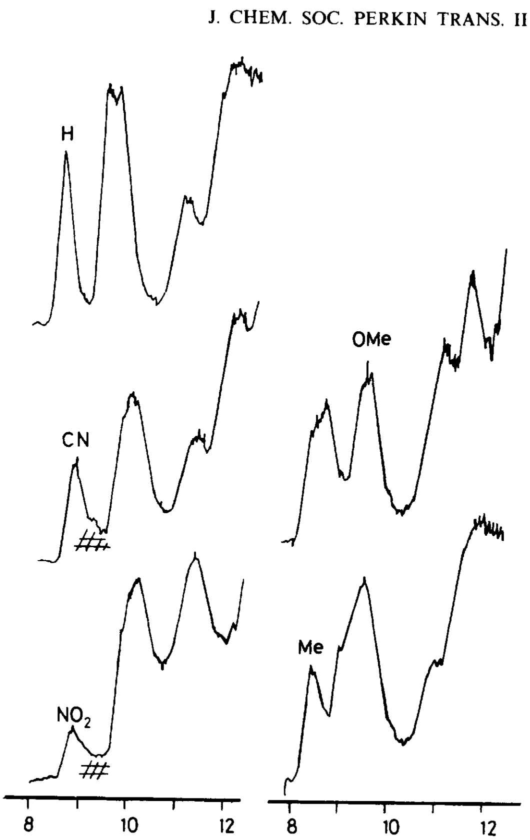


Figure 1. He^I p.e. spectra of *para*-substituted ω-ethylthioacetophenones, $YC_6H_4COCH_2SC_2H_5$

For both compounds, the α 0° rotamers are more stable than the α 90° ones by about 1.2—12 kJ mol^{-1} depending on the β value. This result is in contrast with the conclusions reached from the analysis of i.r. and u.v. data which indicate that the *gauche* conformers predominate in solution.[5] Considering that the geometry has not been optimized and that the basis set is rather limited, it is unwise to attach quantitative meaning to these data. We shall see, however, that the computational results are in agreement with the gas-phase p.e. spectral data.

Photoelectron Spectra.—Figure 1 presents the low (8—12 eV) energy region of the p.e. spectra of ω-ethylthioacetophenones (**1**)—(**5**). The IE values thus obtained are shown in the partial energy level diagrams of Figure 2.

The compounds studied derive from the corresponding acetophenones, YC_6H_4COMe, by substitution of an SEt group for an ω-hydrogen atom. The close similarity of the electronic structures is expected to give rise to similar p.e. spectra, apart from bands related to MOs mainly localized at the ω substituent. Below 11 eV, the p.e. spectra of acetophenones are formed by three ionization processes resulting in partially resolved bands when Y = OMe, H, and CN and an unresolved structure for Y = NO_2.[1] Two ionizations are related to the π_s and π_a benzene MOs, the former also containing contributions from the π(CO) and Y-localized MOs. The third one derives from the *n*(CO) orbital. Ionization from MOs mainly localized at Y (≠ H) gives rise to bands above 11 eV.

The presence of the alkylthio substituent is expected to generate, in the energy region of interest, a low IE band at 8—9

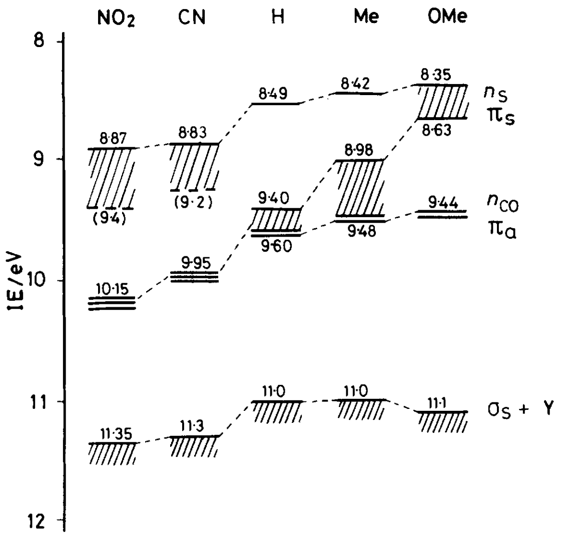


Figure 2. Experimental (p.e. spectra) partial energy level diagrams (eV) for *para*-substituted ω-ethylthioacetophenones, $YC_6H_4COCH_2SC_2H_5$

Table 2. π_s IE values (eV) of *para*-substituted acetophenones and their ω-iodo and ω-ethylthio derivatives $YC_6H_4COCH_2X$

Y \ X	H[a]	SEt	I[a]
NO_2 (**1**)	10.05	10.15	9.59
CN (**2**)	9.9	9.95	9.54
H (**3**)	9.38	9.4	9.21
OMe (**5**)	8.52	8.63	8.60

[a] From ref. 1.

eV and a higher IE band at about 11 eV ascribed to ionization from the n_S and σ_S orbitals, respectively.[17] Figures 1 and 2 show that these expectations are fulfilled, and, therefore, the assignment given in Figure 2 follows from the above arguments. The theoretical calculations confirm this assignment, predicting, in the lowest IE region of the spectra, the presence of the MOs expected on an experimental basis including the stabilization observed on going from Y = H to Y = NO_2. In particular, on going from Y = H to Y = NO_2 the calculations predict a stabilization of the HOMO by 0.30—0.35 eV and of the π-ring orbitals by 0.82—0.87 eV depending upon the conformation. These figures are to be compared with the experimental stabilizations of 0.38 (HOMO) and 0.74 (π_s) eV. The comparison of the experimental shift of the second π-ring orbital is hampered by the overlap of the π_a and *n*(CO) bands in the spectra. (The calculations, however, wrongly predict that the carbonyl lone pair orbital lies close to the second sulphur lone pair σ_S). The calculations, therefore, confirm the assignment of the p.e. spectra and in particular the high localization of the HOMO at the sulphur atom and, when Y = H or an electron-withdrawing substituent, the absence of any other MO (in the Koopmans' approximation) closer than 1 eV to the HOMO.

The first band in the spectrum of ω-ethylthioacetophenone, (**3**), has the typical sharp aspect of a non-bonding sulphur lone pair (see Figure 1). The variation of the Y substituent has two effects on the appearance of the spectra. (i) The energy of the π_s band changes by 1.5 eV on going from Y = NO_2 to Y = OMe due to the inductive and mesomeric effect of the substituent, while the HOMO energy decreases by only 0.5 eV because it experiences almost exclusively the inductive effect of Y. These different shifts cause a partial overlap of the two bands when Y is an electron-releasing substituent. This hinders the observation of the shape and relative intensity of the n_S band in compounds (**4**) and (**5**) (see Figure 1); (ii) When Y is an electron-withdrawing substituent, the intensity of the n_S band decreases dramatically with respect to the following composite band [due to π_s, π_a, and *n*(CO) ionizations], while a shoulder appears on its high IE side centred at about 0.4 (**2**)—0.5 (**1**) eV from the main peak.

As reported above, no other bands are expected in this energy region, either from experimental or theoretical considerations. More than one band from a given MO (in a closed-shell molecule) can be due either to two-electron processes (ionization of one electron accompanied by excitation of a second valence electron[18]) or the presence of more rotamers in which conjugation of the relevant MO changes significantly with conformation.[19–21] Two-electron processes have never been observed in the low-energy region of u.v. p.e. spectra, while the splitting of an n_S band with conformation has been reported several times. In all such cases, however, the sulphur atom is directly bonded to a π-system[6,22,23] and, therefore, even small rotation around the interconnecting bond may produce significant variation of the n_S—π conjugation. In ω-ethylthioacetophenones, however, sulphur is not bonded to an unsaturated atom, making the present case different from those previously reported.

Discussion

Examination of the p.e. spectral data has allowed us to consider whether the results are in better agreement with the planar conformation (α 0, β 0°) of the gas phase as indicated by the theoretical calculations or with the *gauche* conformation suggested by i.r. and u.v. absorption spectra in solution (α *ca.* 90°).

In Table 2 the π_s IE values of compounds (**1**)—(**3**) and (**5**) are compared with those of the corresponding *para*-substituted acetophenones and ω-iodoacetophenones.[1] The IEs of the thio derivatives are equal or slightly (*ca.* 0.1 eV) higher than those of the corresponding acetophenones. If an important π—σ (C–S) hyperconjugative interaction were present it would have destabilized the π_s IE value.[24–26] This interaction, however, is possible only if α is significantly larger than 0°. The lack of evidence for hyperconjugative interaction in the ^{13}C n.m.r. spectra of the methylene carbon has been ascribed[27] to a $\pi \longrightarrow S\,(3d)$ orbital interaction which induces a charge transfer (CT) in the direction opposite to hyperconjugation. The p.e. spectra of thiobenzenes[24–26] indicate, however, that hyperconjugation prevails over the $\pi \longrightarrow S(3d)$ CT. In addition, calculations indicate that sulphur 3*d* orbital mixing with the HOMO, the two uppermost π, and the three lowermost π* orbitals is negligibly small in both compounds (**1**) and (**3**) for all the α and β values considered. The close parallelism between corresponding π_s IE values for X = H and SEt indicate, therefore, that in the gas phase the angle α is close to 0°.

When α 0° and β 0° the n_S orbital is parallel to the π-orbitals. Rotation around the C–SR bond brings the sulphur lone pair into the main molecular plane (for β 90 and 270°) where the *n* (CO) orbital lies. This produces an increase in the total energy (see Table 1) deriving also from lone pair–lone pair repulsion. This interaction is destabilizing for n_S, which has higher energy than *n*(CO). Therefore, the shoulder on the high IE side of the n_S band cannot be ascribed to rotamers deriving from variation of the angle β when α is 0°. We can conclude, therefore, that the main n_S peak derives from a group of conformers whose angles α and β are both close to 0°.

Rotation around the O(C)–C(SR) bond (variation of angle α) breaks the through-bond interaction[28] between the n_S and the (lower-lying) π-orbitals, producing a stabilization of the HOMO (mainly n_S). In agreement, the calculations predict that the HOMO is at higher IE by *ca.* 0.3 eV for α 90 than 0° (for all

β values and both Y substituents). This stabilization energy compares favourably with the energy separation (0.4—0.5 eV) between the main n_S peak and its high-energy shoulder in the spectra of compounds (**1**) and (**2**).

In both derivatives (**1**) and (**3**), the calculations indicate that for α 90° the lowest-energy minima occur at β 225 and 90° (see Table 1). In these conformations the sulphur lone pair points towards the carbonyl group allowing a through-space[28] interaction with its π and π^* orbitals.[29,30] The lowest values of the total energy at these angles indicate that the $\pi^* \longleftarrow n_S$ CT interactions prevail over those between filled orbitals (π_s and n_S). Electron-withdrawing substituents not only inductively lower the π^* orbitals, but introduce an additional low-lying π^* orbital localized also at the phenyl and carbonyl groups[31] facilitating the CT interaction. As a consequence, conformers with α 90° and β 225 and 90° are stabilized in compounds (**1**) and (**2**). This effect is reminiscent of that observed in ω-halogenoacetophenones, but significantly smaller. Table 2 indicates, in fact, that the difference between the π_s IE values of the iodo- and thio-derivatives increases with the electron-withdrawing capability of the *para*-substituent. In the iodo derivatives the two equivalent 5*p* lone pair orbitals assume a doughnut-shaped distribution which renders immaterial the value of β. In the thio derivatives, instead, the through-space $n_S \longrightarrow \pi^*$ (CO) interaction is maximized for selected β values. Since the activation energy values for the rotation around the (O)C–C(SR) and C–SR bonds are quite small (see Table 1) a distribution of rotamers exists which produces the splitting of the first band[32] in the derivatives where an electron-withdrawing substituent favours the CT interaction.

Conclusions

Combined analysis of the p.e. spectra and theoretical results indicates that ω-ethylthioacetophenone, and possibly its *para*-derivatives bearing electron-releasing substituents, adopt a planar conformation (α, β, and γ 0°) in the gas phase. The HOMO is the sulphur lone pair orbital which is parallel to the π-orbitals with which it slightly interacts through bond, that is *via* a small mixing with the CH_2 bridge.

This same conformation is also the most probable for the derivatives bearing an electron-withdrawing substituent. In this case, however, the presence of a low-lying empty orbital and the small barrier to internal rotation also stabilize conformers with the angle α largely different from 0° and β close to 225 and 90°.

These results are in contrast with those obtained in solution (i.r. and u.v. measurements) where the *gauche* conformation predominates. The most obvious explanation for this difference, namely, that the *gauche* conformation is stabilized by solvation, seems to disagree with the small variation of the *cis–gauche* ratio observed on changing the solvent polarity.[5] However, ^{13}C n.m.r. spectra (in solution) is in accord with the present analysis; such spectra fail to show the effect of strong hyperconjugation reported for the halogen derivatives,[27] but rather follow an opposite trend parallel to that of acetophenones.[5]

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