Ab Initio and Electron Spectroscopy Study of Carbonyl Derivatives†

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The bands present in the low ionisation energy region ($E_i \leqslant 12$ eV) of the He I photoelectron spectra, and the low energy resonances of the electron transmission spectra of some substituted carbonyls XC(O)R (X = Et_2N, alkyl, EtS and EtO; R = Me and CH_2SR) have been assigned to the corresponding molecular orbitals by comparison with the assignments reported for simple related molecules. Fully optimized 3-21G *ab initio* calculations reproduce the assignment of the spectra and available geometric parameters and therefore have been used to determine the electronic charge distribution among the various atoms and groups in the studied compounds. A combined analysis of the theoretical and experimental data provides a detailed understanding of the electronic interaction among the X, CO and R groups in the molecules studied.

Within the context of a UV-photoelectron spectroscopy and theoretical study of the electronic and geometric structure of carbonyl derivatives,[1-4] we recently reported[5] preliminary results on the electronic interactions present in (alkyl/aryl)-sulfonylmethyl ketones, $RC(O)CH_2SO_2R'$, based on the X-ray diffraction analysis of one compound (R = $MeOC_6H_4$, R' = Et) and on the PE spectra and the results of semi-empirical calculations on several model systems. It was found that there is a large interaction between the carbonyl and the sulfonyl groups as shown by eigenvector analysis and energy shifts (with respect to reference compounds) of the ionization energy values related to orbitals mainly localized at the two interacting groups. These compounds adopt a conformation in which the partially positively charged S and carbonyl C atoms are closer than the sum of the van der Waals radii to the partially negatively charged sulfonyl and carbonyl O atoms, respectively. The carbonyl C–sulfonyl O interaction partially counterbalances the $-I_{SO_2}$ effect, and is responsible for the fact that the SO_2R group can donate electrons towards the carbonyl group more strongly than an alkyl group.[5]

To gain a deeper insight into this rather uncommon behaviour of the sulfonyl group, we have undertaken a multidisciplinary study of (alkyl/aryl)sulfonylmethyl ketones $RC(O)CH_2SO_2R'$ bearing different substituents; *viz.* R = R_2N, RS, RO, alkyl and aryl, R' = alkyl and aryl. As a preliminary part of this work, we present here the experimental data together with theoretical results obtained on simpler, related molecules. In particular, we have determined the valence ionisation (E_i) and attachment energy (E_A) values by means of photoelectron (PE) and electron transmission (ET) spectroscopies, respectively, and computed the corresponding energy levels, the goemetry and the electron charge distribution by means of 3-21G* calculations.

The compounds analysed are listed below: compounds **1**–**8** and **1**–**8a** were used, respectively, for the spectroscopic and theoretical investigations.

This approach allows one to determine separately the interaction of the heterogroup (X) and of a β-S atom in a *gauche* orientation with the carbonyl group. The available IR[6-8] data and molecular mechanics calculations (only on **6**),[9] indicate that in the compounds **5**–**8**, the most stable rotamer is a *gauche* one.

1	$Et_2NC(O)Me$	**1a**	$Me_2NC(O)Me$
2	EtC(O)Me	**2a**	EtC(O)Me
3	EtSC(O)Me	**3a**	MeSC(O)Me
4	EtOC(O)Me	**4a**	MeOC(O)Me
5	$Et_2NC(O)CH_2SMe$	**5a**	$Me_2NC(O)CH_2SMe$
6	$EtC(O)CH_2SMe$	**6a**	$EtC(O)CH_2SMe$
7	$EtSC(O)CH_2SMe$	**7a**	$MeSC(O)CH_2SMe$
8	$EtOC(O)CH_2SMe$	**8a**	$MeOC(O)CH_2SMe$

Experimental and Calculations

Photoelectron (PE) Spectra.—The He I spectra were recorded on a Perkin-Elmer PS-18 photoelectron spectrometer connected to a Datalab DL4000 signal analysis system. The bands, calibrated against rare-gas lines, were located using the positions of their maxima, which were taken as corresponding to the vertical E_i values. The accuracy of the E_i values was estimated to be better than ±0.05 eV (except for shoulders).

Electron Transmission (ET) Spectra.—ET spectroscopy allows determination of the energy at which electrons are temporarily captured by an atomic or molecular species in the gaseous phase (attachment energy, E_A). These E_A values are, to a first approximation, the negative of the vertical electron affinities (E_{ea}) of the capturing species. Our apparatus (see ref. 10 for more details) is in the format devised by Sanche and Schulz.[11] The derivative of the transmitted current is recorded as a function of the incident electron energy. ET spectra were obtained by using the apparatus in the 'high rejection' mode, yielding a signal which can be related to the near total electron scattering cross section.[12] The E_A values reported correspond to the vertical midpoints between the minima and the maxima of the differential signal. The energy scales were calibrated by using the $(1s^12s^2)$ ^2S anion state of He. The estimated accuracy is ±0.05 or ±0.1 eV, according to the number of decimal places reported.

Calculations.—The energy and the localisation properties of the relevant molecular orbitals (MOs), the electron charge

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† Non-SI unit employed: 1 eV = 96.4853 kJ mol^{-1}.

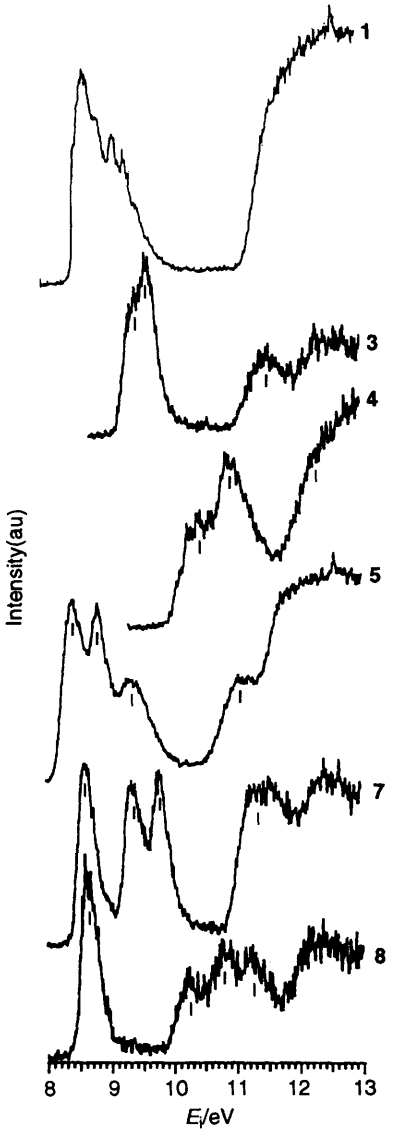


Fig. 1 He I PE spectra of compounds **1**, **3**–**5**, **7** and **8**

distribution at the various atoms and/or groups, and the geometric parameters were computed at the *ab initio* 3-21G* level using the GAUSSIAN 92 series of programs.[13] All the parameters were allowed to vary independently in the optimization procedure. The present 3-21G* calculations reproduce the available experimental geometries,[14–16] rationalise the ν_{CO} stretching frequency trends and reproduce (assuming the validity of Koopmans' Theorem) the assignments in the spectra. They can, therefore, be used with confidence to obtain the electron charge distribution on the various atoms and groups of the compounds studied.

The calculations were performed at the Cineca Computing Center in Bologna, Italy. The compounds examined were available from previous studies.[9,10,17,18]

Results and Discussion

The He I PE and ET spectra of compounds **1**, **3**–**5**, **7** and **8** are shown in Figs. 1 and 2, respectively; the spectra of compounds **2** and **6** have been previously obtained.[1] The E_i and E_A values are shown in the partial energy diagrams of Figs. 3 (**1**–**4**) and 4 (**5**–**8**). Figs. 5 and 6 present partial correlation diagrams for the highest occupied and lowest virtual energy levels in compounds **1**–**4a** and in the *cis* and *gauche* rotamers of compounds **5**–**8a**, respectively, obtained by 3-21G* calculation. The computed bond distances are listed in Table 1, while the computed charges at the various atoms and/or groups are presented in Table 2.

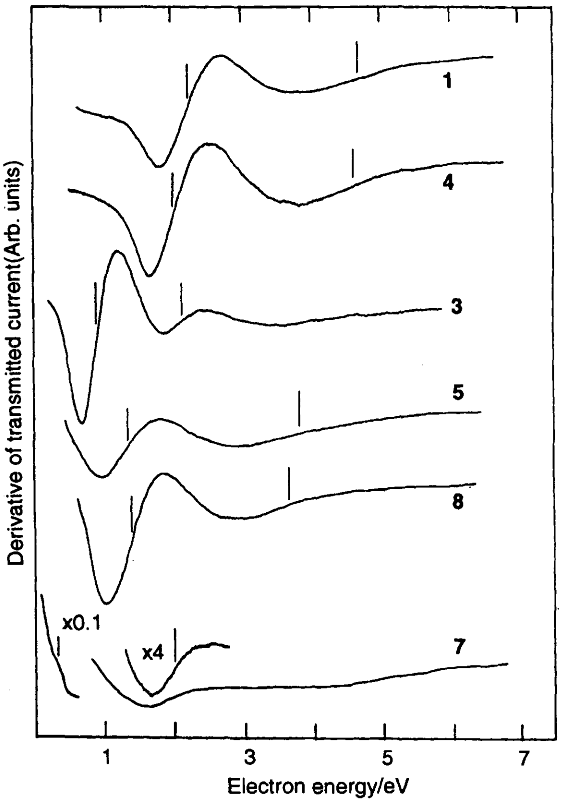


Fig. 2 Derivative of the electron current transmitted through gas-phase compounds **1**, **3**–**5**, **7** and **8**

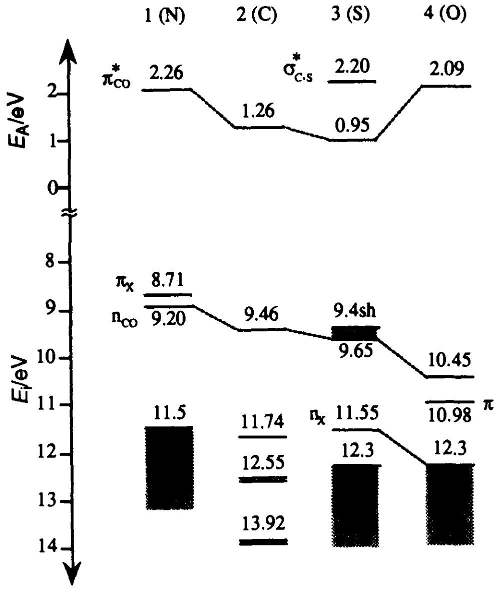


Fig. 3 Correlation diagram of the experimental E_i and E_{ae} values in compounds **1**–**4**

We shall discuss first the geometry of the studied compounds, then the filled and empty energy levels, and, finally, the above data will be discussed together with the electron charge distributions.

The calculations indicate that compounds **1**–**4a** are planar, in agreement with electron diffraction data on **4a**[15,16] and the conclusions reached from the results of MM[19] or STO-3G[20] calculations on **1a** and the analysis of the IR spectra of **1a** and **2a**.[21]

Table 1 Lengths of the bonds formed by the carbonyl carbon atom in compounds **1–8a** obtained by *ab initio* 3-21G* calculations, sum of mean covalent radii and carbonyl stretching frequencies

	ab initio 3-21G*/Å			Sum of covalent radii/Å		
Compd. (X)	d_{C-O}	d_{C-X}	d_{C-C}	d_{C-O}	d_{C-X}	$\nu_{CO}(CCl_4)/cm^{-1}$
X–C(O)Me						
1a (N)	1.222	1.362	1.519	1.231	1.346	1656[b]
2a (C)	1.211	1.516	1.514	1.210	1.511	1719[c]
3a (S)	1.208	1.773	1.513		1.762	1695[d]
4a (O)	1.203	1.354	1.500	1.196	1.336	1741[e]
X–C(O)CH$_2$SMe (*gauche*)						
5a (N)	*1.221*	*1.349*	*1.527*			*1644*[b]
6a (C)	*1.210*	*1.514*	*1.525*			*1711*[c]
7a (S)	*1.208*	*1.767*	*1.520*			*1679*[d]
8a (O)	*1.207*	*1.345*	*1.504*			*1732*[e]

[a] Ref. 17. [b] Ref. 19. [c] Ref. 18. [d] Ref. 9. [e] Ref. 7.

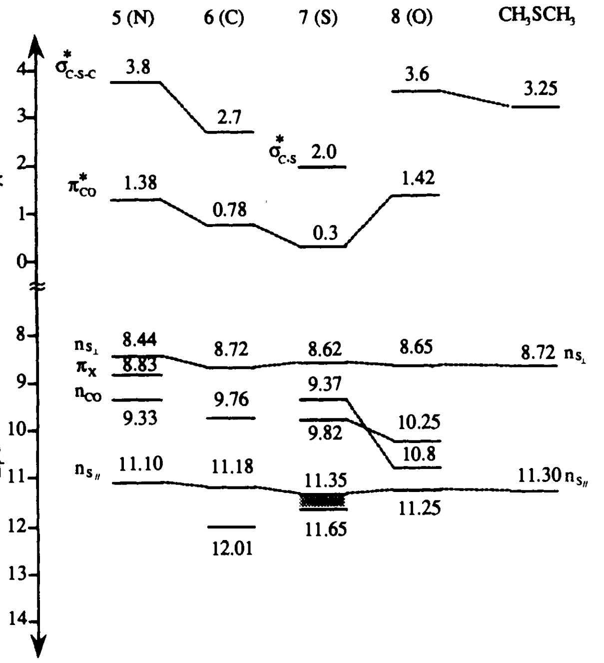


Fig. 4 Correlation diagram of the experimental E_i and E_{ae} values in compounds **5–8**

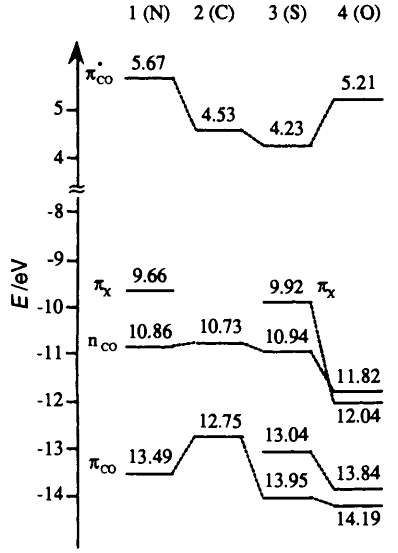


Fig. 5 Correlation diagram of the highest occupied and the lowest vacant orbital energies computed at the *ab initio* 3-21G* level for compounds **1–4a**

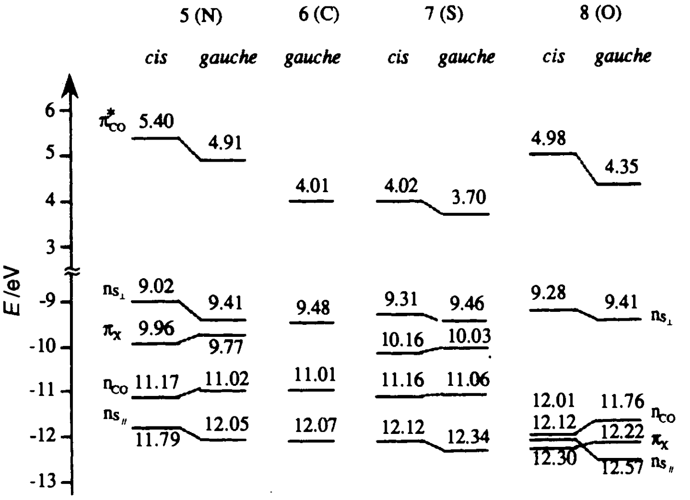
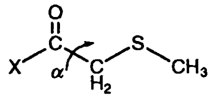


Fig. 6 Correlation diagram of the highest occupied and the lowest vacant orbital energies computed at the *ab initio* 3-21G* level in the *cis* and *gauche* rotamers of compounds **5–8a**

The IR spectra[7,9,18,19] of compounds **5**, **7** and **8**, and the results of molecular mechanics calculations[6] on **6**, indicate that these compounds prefer a *gauche* conformation, but they may also have a less stable *cis* conformation. The *ab initio* 3-21G* computations indicate that **6a** has only one stable conformation (*gauche*, α = −106.69°) and that compounds **5a**, **7a** and **8a** possess two stable rotamers, *cis* and *gauche* [α = −76.50° (O), −106.10° (N) and −108.91° (S)].



The *gauche* rotamer is the more stable one for **8a** by 8.35 kJ mol^{-1}, but the less stable one for **5a** and **7a** by 2.81 and 9.36 kJ mol^{-1}, respectively. We shall see later, however, that the spectral data agree better with a *gauche* conformation for all the derivatives **5–8**.

Table 1 lists the lengths of the bonds (d_{C-O}, d_{C-X} and d_{C-C}) involving the carbonyl carbon atoms in compounds **1–8a** obtained from the calculations, together with the sums of the available d_{C-X} and d_{C-O} mean covalent radii,[17] and their IR carbonyl region stretching frequencies, ν_{CO}.[7,9,18,19] The computed bond distances agree well with those obtained by electron diffraction[15] for **4a** and by *ab initio* calculations for **4a** (4-31G)[22] and **1a** (STO-3G).[21] Good linear correlations exist

Table 2 Charges at various atoms and groups (*e*) for compounds **1**–**8a** obtained by *ab initio* 3-21G* computations (a minus sign indicates an excess of negative charge)

		Carbonyl		
Compd. (X)	X	C	O	Me
X–C(O)Me				
1a (N)	−0.249	0.866	−0.639	0.021
2a (C)	−0.002	0.536	−0.554	0.020
3a (S)	0.157	0.349	−0.559	0.053
4a (O)	−0.32	0.858	−0.611	0.073
X–C(O)CH$_2$SMe (*gauche*)				CH$_2$SMe
5a (N)	*−0.228*	*0.881*	*−0.628*	*−0.025*
6a (C)	*−0.134*	*0.542*	*−0.538*	*0.130*
7a (S)	*0.219*	*0.356*	*−0.550*	*0.007*
8a (O)	*−0.305*	*0.899*	*−0.619*	*0.025*

between the computed and experimental d_{C-O} and d_{C-X} values of Table 1, supporting the computed bond distances. In both series, the increase in d_{C-O} is accompanied by a lowering of the ν_{C-O} value. The anomalies of compounds **3** and **7** in the linear correlations can be ascribed to a mechanical coupling between the C=O and C–S oscillators, which decreases the ν_{C-O} values with respect to the corresponding ketones.[23,24]

In compounds **5**–**8a**, the d_{C-X} and d_{C-C} values are slightly shortened and slightly lengthened, respectively, relative to the corresponding data for compounds **1**–**4a**. In the oxygen derivatives, in addition, the d_{C-C} bond distance is shorter than in the other congeners. These findings can be rationalised in terms of a variation of electron charge distribution caused by substitution and will be discussed below.

UV PE and ET Spectra of Compounds **1**–**8**.—A comparison with the assignment reported for simple related molecules and an analysis of relative band intensity[25–30] indicates that the first three (two for **1**) bands present in the low ionisation energy region of the PE spectra of compounds **3** and **4** can be related (see Fig. 3) to ionisation from the carbonyl lone pair orbital (n_{CO}) and the two MOs mainly localized at the heteroatom lone pair perpendicular to (π_X) and lying in the molecular plane (n_X). Band overlap presented the π_{CO} band to be located in the spectra. The energy ordering **2** > **1** > **3** > **4** suggested by the computations is in line with experimental data for related molecules.[1,31,32]

The low E_A resonance present in the spectrum of **2** has been ascribed[1] to electron capture into the π^*_{CO} MO. The substitution of an EtO or Et$_2$N group for an alkyl group causes a large destabilisation of the π^*_{CO} MO because of a $\pi^*_{CO} \leftarrow \pi_X$ charge transfer (CT) interaction larger than that in the alkyl derivatives and a lack of empty orbitals corresponding to the σ^* orbitals of the alkyl groups.

The smaller E_A value of **3** with respect to **1** and **4** is ascribed to the larger carbon–heteroatom interatomic distance and the larger size of the 3p compared with the 2p orbitals, leading to a smaller π^*_{CO}–π_X overlap, and to the presence of low-lying d orbitals in the third-row element.[33–36] There is no contribution from σ^*_{C-S} orbitals because of the planarity of the molecule. The energy and the low intensity of the second resonance (2.2 eV) in the ET spectrum of **3** corresponds to that observed in the spectrum of other sulfides.[37–39] This has been ascribed on the basis of experimental and theoretical evidence to electron capture into a σ^*_{C-S} MO.

That compound **1** has the highest π-electron polarizability in the series is in agreement with the following observations. It has the largest π-charge delocalization indicated by the largest $\pi^*_{CO} \leftarrow \pi_X$ charge transfer, accompanied by the largest charge separation between the atoms of the carbonyl group. In fact, in the *O*-protonated derivatives of amides and (*S*-alkyl thio)esters, the charge at the oxygen atom increases with respect to the neutral molecules by ≈0.4–0.5 *e*.[40] This charge derives mainly from the carbonyl atom in the oxygen and sulfur derivatives, but mainly from the X atom in the nitrogen derivatives. The lower n_{CO} E_i value of **1** relative to **2** probably derives from the higher polarizability of this compound.

Two new bands (E_{i1} and E_{i4}) are present in the low E_i region of the PE spectra of compounds **5**–**8** with respect to the spectra of the acetyl derivatives and an additional resonance appears in the ET spectra of **5**, **6** and **8** at 2.7–3.8 eV (the corresponding resonance is not visible in the spectrum of **7**, probably because of the low signal intensity). These features are clearly related to ionisation from, and electron capture into, MOs mainly localized at the CH$_2$SMe fragment (see Fig. 4, where $n_{S\perp}$ and $n_{S\parallel}$ are the sulfur lone pair orbitals perpendicular to, and lying in, the C-S-C plane, respectively).[1,4,41]

The through-space and through-bond interactions between the orbitals of the X–C(O) (n_{CO} and π_X) and CH$_2$SCH$_3$ ($n_{S\perp}$ and $n_S{}^4{}_{\parallel}$) groups are destabilising for the $n_{S\perp}$ MO, which is the HOMO. The destabilisation is barely visible (see Fig. 4), probably because of the sizeable electron-withdrawing inductive effect of the X–C(O) groups.[42]

A comparison of the experimental E_i values with the *ab initio* energy levels for the *cis* and *gauche* rotamers indicates that the gas-phase conformation of these compounds is the *gauche* one, in agreement with results of IR studies[7,9,18,19] and in good agreement with the *ab initio* total energy reported above for **6a** and **8a**, but in disagreement for **5a** and **7a**. This failure is probably related to the small basis set used.

The prevalence of the *gauche* conformation in the gas-phase is also strongly supported by the ET spectra. In fact, the lowest energy resonance, ascribed to electron capture into the π^*_{CO} MO, is stabilised by 0.5–0.9 eV with respect to the corresponding resonance in the spectra of compounds **1**–**4**. This stabilisation, due to π^*_{CO}–σ^*_{C-S-C} mixing, is possible only in the *gauche* rotamer, and it is larger for **5** and **8** because of the smaller energy gap between the two interacting orbitals. In fact, the σ^*_{C-S-C} resonance appears at higher energy in the spectra of **5** and **8**.

The resonance at 2 eV in the ET spectrum of **7** is related to the σ^*_{C-S} orbital of the *S*-alkyl thioester group and corresponds to that present at 2.2 eV in the spectrum of **3**.

The calculations reproduce with high accuracy the E_i and E_A trends from the experimental data.

Total Electron Charge Distribution.—Table 2 lists the charges on the various atoms or groups of the molecules **1**–**8a** obtained by the *ab initio* calculations. A minus sign indicates an excess of negative charge. Different levels of computations give different absolute charges, therefore, we do not attach a quantitative meaning to the various computed charges, but rather to their differences from one molecule to another. We discuss first the acetyl derivatives **1**–**4a** and relate charge density changes with the variations in bond distance, energy level and IR ν_{CO} values.

In the carbon derivatives, **2a** about 0.5 *e* is transferred from the carbon to the oxygen atom of the carbonyl group, while the X and Me groups are nearly neutral. With respect to **2a**, the charge density increases and decreases sizeably at the X group and at the carbonyl C atom, respectively, in both **1a** and **4a**, decreases slightly at the methyl group of **4a**, and increases at the carbonyl oxygen atom of both molecules. According to Libit and Hoffmann,[43] a donor substituent polarizes a double bond towards the unsubstituted atom. The polarization can be traced back to the larger electronegativity of the heteroatoms with respect to the carbon atom of an alkyl group and to a mixing of the π and π* orbitals of the double bond with the interacting orbitals of the substituent. In the nitrogen derivative, the low $E_i(\pi_X)$ value favours a large charge transfer toward the π^*_{CO} MO, in agreement with the high E_A value, the large electron charge density at the carbonyl O atom and the low ν_{CO} value. The large $-$I effect of the alkoxy group in **4a** attracts negative charge from the rest of the molecule more than the amino group does in **1a**. This effect is not compensated by the $\pi^*_{CO}\leftarrow\pi_X$ CT interaction because $E_i(\pi_X)$ in **4a** is larger than in **1a**. Consequently, in **4a** the negative charge density at the carbonyl O atom and at the Me group decrease, the d_{C-C} and d_{C-O} bond distances decrease and the ν_{CO} value increases with respect to **1a**.

The charge distribution in **3a** seems to indicate that the largest difference with respect to the alkyl derivative **2a** is the $+$I effect of the substituent which increases charge density at the carbonyl C atom.[40]

In the *gauche* rotamers, the CH_2SMe group in **6a** bears a positive charge. However, when X is a good donor, the CH_2SMe group is nearly neutral. In other words, the two substituents, X and CH_2SMe, compete with each other in donating charge to the carbonyl group, and only when X is an alkyl group, which has moderate donor properties, can the CH_2SMe group fully display its hyperconjugative electron donating capability.

At the same time, the charge densities at the X group ($X \neq R$) and the carbonyl C atom decrease with respect to the acetyl derivatives. These variations, larger in the *cis* derivatives, can be ascribed to a (small) increase of the conjugation between the X and the carbonyl groups, which transfers charge to the latter, and to a simultaneous charge transfer from the π_{CO} MO towards the vacant σ^*_{C-S-C} orbital. This hypothesis is confirmed by a decrease and increase in the d_{C-X} and d_{C-C} bond distances, respectively, relative to compounds **1–4a**.

Conclusions.—The π_X, n_{CO}, n_X, $n_{S\perp}$ and $n_{S\parallel}$ E_i values, together with the π^*_{CO} and σ^*_{C-S-C} E_A values obtained from the PE and ET spectra of compounds **1–8** give information on the extent of mixing of the various group orbitals. The fully optimized 3-21G* calculations reproduce the available bond distances and the ordering and localisation properties of filled and empty MOs obtained experimentally for compounds **1–4**. They also reproduce the planar conformation of these compounds and the *gauche* conformation of **6a** and **8a**. The computed total energy, however, does not correctly predict (probably because of the small basis set used) that the *gauche* conformation is also the most stable for **5a** and **7a**. The computed energy levels for the *gauche* rotamers of **5–8a** do, however, fit the measured E_i and E_A values much better than the *cis* values.

The variation in the series of the $\pi^*_{CO}\leftarrow\pi_X$, $\pi^*_{CO}-\sigma^*_{C-S-C}$ and $\pi_{CO}-\pi_X$ interactions (and the inductive effect) invoked to rationalise the experimental E_i and E_A trends fully agrees with the eigenvector analysis and the variations of the bond lengths and electron charge distribution obtained by the *ab initio* calculations.

In summary, a combined analysis of the experimental and theoretical MO energies and localisation properties, and the computed bond distances and charge distributions and their variations along and between the two series of compounds indicate that: (*i*) in the nitrogen and oxygen derivatives the, $-I_X$ effect attracts charge from the COY ($Y = Me$ or CH_2SR) group towards the X group; (*ii*) the negative charge on the carbonyl O atom, however, increases with respect to the carbon derivative because of the mixing of the π_X with the π_{CO} and π^*_{CO} orbitals: (*iii*) when $X = S$, the substituent acts as a moderate electron donor group; (*iv*) the CH_2SR group (in the *gauche* conformation) is an electron donor substituent only when X is an alkyl group, otherwise it acts as an acceptor; and (*v*) this causes an increase in the $\pi^*_{CO}\leftarrow\pi_X$ CT interaction with respect to the corresponding acetyl derivatives.

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