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ELECTRON AFFINITIES OF DOUBLE BOND π^* ORBITALS DETERMINED BY MEANS OF ELECTRON TRANSMISSION SPECTROSCOPY

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Abstract - The electron transmission spectra of small molecules containing C=C, C=N, C=O, C=S and N=N double bonds are reported. The electron affinities of these functional groups, associated with electron capture into their empty π^* orbitals, are discussed in terms of heteroatom electronegativities, geometrical variations and localization properties of the π^* orbitals.
The largest electron acceptor properties were observed in the thioketone derivative, which generates a stable Π anion state. The ionization energy values relating to the heteroatom lone pair and the filled π orbitals are also reported.

Over the last few decades many attempts have been made to correlate chemical reactivity with the electronic structure of the reactants. A simple and successful approach to this problem has been provided by "frontier molecular orbital" theory[1], which points out the kinetic and stereoselective dependence of a reaction upon the energy and wavefunction coefficients of both the highest occupied and lowest unoccupied molecular orbitals (MO's). Within the context of Koopmans' theorem[2], the energies of the filled valence MO's can be determined by means of ultraviolet photoelectron spectroscopy (UPS)[3], which has provided a wealth of ionization energy (IE) data. In contrast little of the complementary electron affinity (EA) data, associated with the energy of the empty MO's, are available.

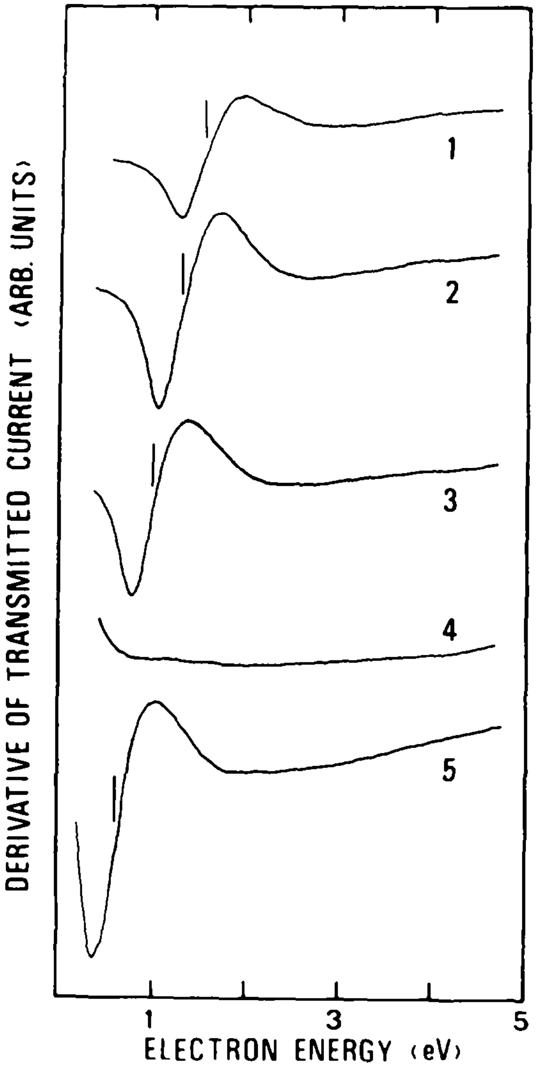
One of the most powerful means for the determination of the various EA's of a gas-phase molecular system is electron transmission spectroscopy (ETS)[4,5], in the format devised by Sanche and Schulz[6].

This technique takes advantage of the sharp variations in the total scattering cross-section associated with resonances to measure the energies at which an electron can be temporarily trapped in normally unoccupied MO's. A limitation of ETS is that stable anion states cannot be detected. However, for many molecular systems, even the ground anion state in unstable with respect to autodetachment of the extra electron.

In this paper we report the ETS spactra of small selected molecules containing the double bonds C=C, C=N, C=O, C=S and N=N, in order to measure and compare the EA's of these common organic functional groups.

EXPERIMENTAL

Our ETS apparatus has been previously described[7]. Here we briefly recall that an electron beam, selected in energy by a trocoidal monochromator and alligned by a magnetic field, is directed through a gas-filled collision chamber. Retarding electrodes reject those scattered electrons which have lost a given value of axial velocity.



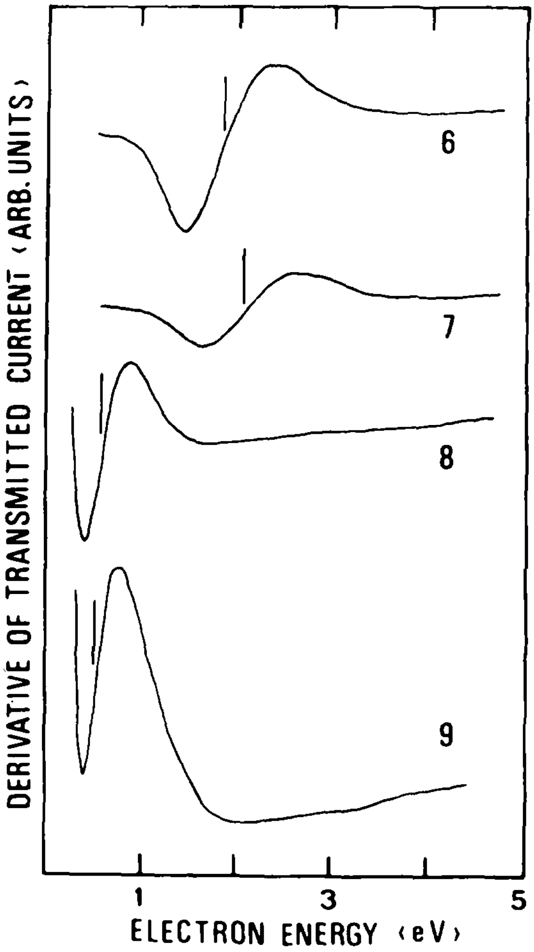


Fig.1 - Derivative of transmitted current as a function of energy for 1,1-ditertbutylethylene(1), ditertbutylimine (2), ditertbutylketone(3), ditertbutylthioketone (4) and trans-azotertbutane (5).

Fig.2 - Derivative of transmitted current as a function of energy for methyl formate (6), N,N-dimethylformamide (7), N,N-dimethylthioformamide (8) and thioacetamide (9).

In order to enhance the resonant scattering cross-section, the first derivative of the transmitted electron current is recorded as a function of the electron impact energy. The vertical midpoint between the minimum and maximum of the derived signal is referred to as the attachment energy (AE) and closely approximates the negative of the vertical EA.

The energy scales were calibrated using the $(1s^1 2s^2)\,^2S$ anion state of helium and the estimated accuracy of the AE values is ±0.05 eV. For completeness, the lowest IE values of the molecules under consideration are also reported. The IE data not taken from the literature (that is, those of $((CH_3)_3C)_2C{=}X$ with X = CH_2, NH, O and S) were measured on a Perkin-Elmer PS18 photoelectron spectrometer in our laboratory, calibrating against the Xe and Ar lines.

Most of the compounds under examination were commercially available. 1,1-ditertbutylethylene[8], ditertbutylimine[9], ditertbutylthioketone[9], and trans-azotertbutane[10] were synthesized according to literature procedures.

RESULTS AND DISCUSSION

Figures 1 and 2 show the ET spectra of 1,1-ditertbutylethylene (1), ditertbutyl imine (2), ditertbutylketone (3), ditertbutylthioketone (4), trans-azotertbutane (5), methylformate (6), N,N-dimethylformamide (7), N,N-dimethylthioformamide (8) and thioacetamide (9). The corresponding AE's together with the IE's from the higher-lying MO's, are given in Figures 3 and 4.

The assignment of the first few bands present in the UPS spectra of compounds 1-4 was carried out as briefly outlined below, taking into account the assignment reported[11-14] for 5-9, the band shape and perturbational arguments. In particular, the band at lowest IE in the spectra of 1 and 3 is expected to derive from π_{CC}(9.03 eV) and n_O (8.92eV) ionizations respectively. The spectrum of 2 was assigned (n_N = 9.05 eV and π_{CN} = 10.4 eV) by comparison with the assignment made for 1 and 5. The assignment of the spectrum of 4 is based on that made for 8 and is confirmed by the sharpness of the first band, the assignment for 4 being n_S = 8.10 eV and π_{CS} = 9.90 eV.

None of the compounds studied have been previously analysed by means of ETS. Their spectra will therefore be discussed in some detail. The EA of the lowest unoccupied MO (π^{*}_{CC}) of the reference molecule (ethylene) is -1.73 eV[15], while ionisation from the highest occupied MO (π_{CC}) occurs at 10.51 eV[3]. The substitution of two hydrogen atoms with two tertbutyl groups, to give 1, has a large destabilising effect (1.5 eV) on the filled π_{CC} MO due to σ_{CC}/π_{CC} hyperconjugation (see Fig.3). In contrast, the empty π^{*}_{CC} MO is stabilised by about 0.2 eV. This finding, in line with our previous results[7], indicates that hyperconjugation of the π^{*}_{CC} MO with the higher-lying σ^{*}_{CC} orbitals of the tertbutyl groups prevails over hyperconjugation with the filled σ_{CC} orbitals.

On going from 1 to 2, the replacement of a CH_2 group of the double bond with the more electronegative NH group stabilises the empty π^{*} MO by about 0.2 eV, while the filled π MO experiences a much larger stabilisation (about 1.4 eV).

Similar IE and EA trends were observed on going from benzene to pyridine[16] and from acetylene to hydrogen cyanide[17]. We have previously rationalised[16] the smaller stabilisation of the empty orbitals in terms of i) their smaller localisation, with respect to the filled MO's, at the most electronegative atom and of ii) the reduction of the C-N bond length. This geometrical variation, in fact, results in a stabilisation of the filled orbitals, which are bonding between the carbon and nitrogen atoms, but affects the empty (antibonding) orbitals in the opposite direction.

Analogous considerations can explain the relatively small stabilisation of the empty π^{*} MO and large stabilisation of the filled π MO observed on going from 1,1-ditertbutylethylene (1) to ditertbutylimine (2) and to ditertbutylketone (3)* (see Fig.3).

We note, in fact, that in the unsubstituted molecules methyleneimine and formaldehyde[18], the heteroatom character of the empty π^{*} MO decreases with increasing electronegativity of the heteroatom. Moreover, the double bond length decreases from 1.337 Å[19] in ethylene to 1.21 Å[19] in formaldehyde. For the C=N double bond an average length of 1.30 Å has been reported[20]. The C-N distance, however, was found to be 1.27 Å in glyoxime[19] and 1.237 Å in benzylideneaniline[21].

On going from 2 to 5, where the second carbon centre of the double bond is also replaced by a nitrogen atom, the EA increase (about 0.7 eV) is sizeably larger than the 0.2 eV occuring upon replacement of the first carbon centre, i.e. on going from 1 to 2. The corresponding stabilisation of the filled MO, in contrast, is smaller.

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* In the UP spectrum of 3, the band associated with the π_{CO} MO is hidden by those arising from σ ionisation events. The IE from π_{CO} MO in acetone, however, is 12.6 eV[13]

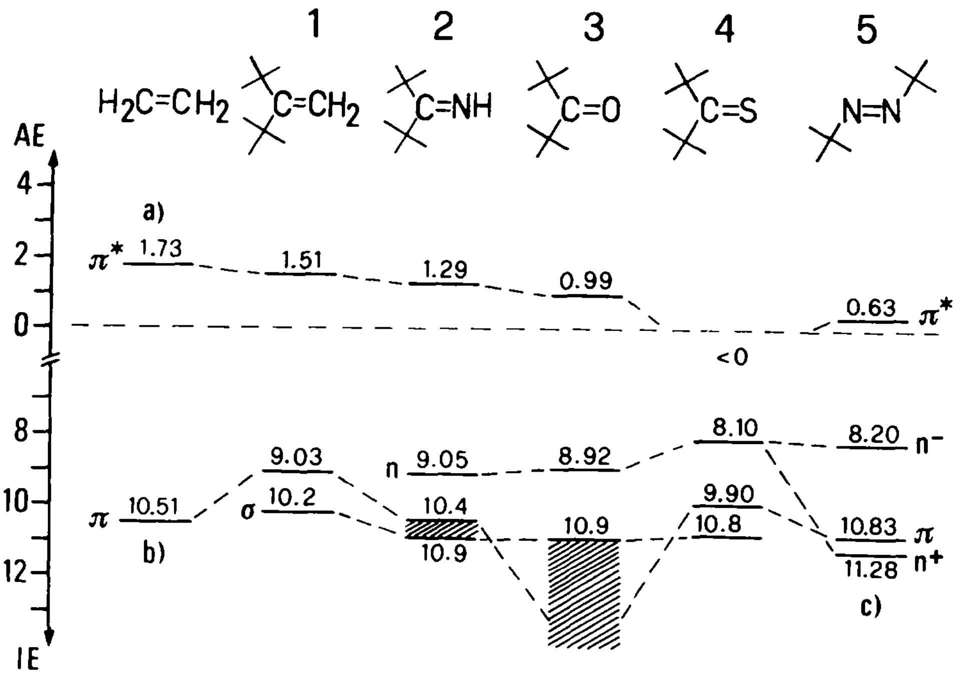

Fig.3- Correlation diagram of the electron attachment and ionisation energies of ethylene and compounds 1, 2, 3, 4 and 5. a) AE taken from reference 15; b) IE taken from reference 3; c) IE's taken from reference 11.

This is consistent with the fact that both the empty π^* MO and the filled π MO of the symmetric double bond must have similar nitrogen character. In addition, upon replacement of the second carbon centre, the bond length variation is probably small (the N=N double bond length is 1.254 Å in CH_3-N=N-CH_3[22]).

As shown in Fig.1, the ET spectrum of ditertbutylthioketone (4) displays no intense resonances in the 0-5 eV energy range. This suggests that electron capture into the π^*_{CS} MO gives rise to a stable anion state. The concomitant stabilisation of this MO and the destabilisation of the filled π_{CS} MO, with respect to the corresponding MO's of the C=NH and C=O double bonds under examination, may stem, in part, from the large C-S bond length (1.71 Å in thioacetamide[19]). However, a large stabilisation of the empty π^*_{CS} MO is consistent with our previous interpretation of the ET spectra of carbonyl [23] and benzene[24] thio-derivatives, recently confirmed by Xα calculations[25], where the stabilisation of the Π anion states was mainly ascribed to π^*/S3d mixing. The participation of the higher-lying S3d orbitals to the formation of the empty π^*_{CS} MO would, in fact, result in a stabilisation of the latter.

Previous ETS investigations[23,24] have shown that charge-transfer interactions with an oxygen or nitrogen lone pair orbital sizeably raises the energy of the empty π^* MO's of proper symmetry. In methylformate (6) and N,N-dimethylformamide (7) these interactions destabilise the π^*_{CO} MO by about 0.9 eV and 1.1 eV respectively, with respect to the π^*_{CO} MO of ditertbutylketone (1) (see Fig.4).

We therefore ran the ET spectra of the methyl-substituted thioimides 8 and 9 in the hope of detecting a resonance above zero energy, associated with the π^*_{CS} MO destabilised by mixing with the nitrogen lone pair. This was indeed the case, as shown in Fig.s 2 and 4. In compounds 8 and 9 the measured AE's were 0.58 and

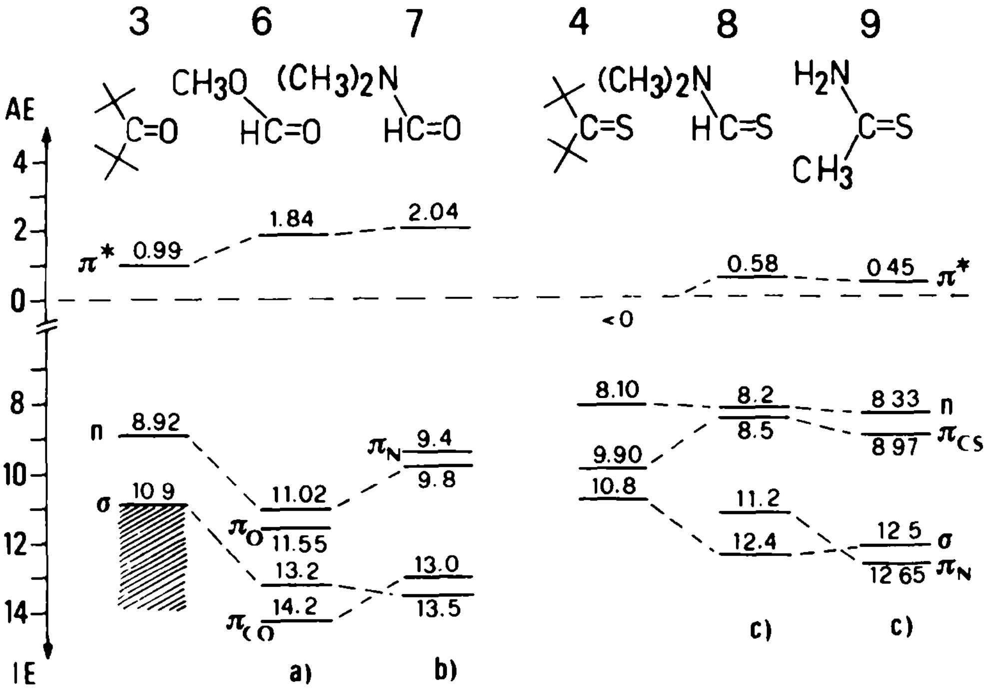

Fig.4- Correlation diagrams of the electron attachment and ionisation energies of compounds 3, 6, 7, 4, 8 and 9.
a) IE's taken from reference 12; b) IE's taken from reference 13; c) IE's taken from reference 14.

0.45 eV respectively, confirming that the Π anion state of ditertbutylthioketone (4) is stable.

Assuming that the size of the wave function coefficients at the carbon atoms of the π^*_{CO} and π^*_{CS} MO's are similar, i.e.,that the energy perturbation caused by the nitrogen lone pair on the carbonyl and thiocarbonyl empty π* orbitals is about the same, the AE's of compounds 7, 8 and 9 would approximately lead to a positive EA of about 0.5 eV for ditertbutylthioketone.

CONCLUSIONS

UPS has shown that the IE from a filled π orbital localised at a C=X double bond rapidly increases with the electronegativity of the X atom.

The present ETS data reveal that the EA's of the corresponding empty π^*_{CX} orbitals increase following the same trend (except for X = S), but are much less sensitive to the nature of the X atom. This result can be rationalised in terms of the opposite effects of the bond length variations on the energies of the filled and empty orbitals under examination, and of the smaller localisation of the latter at the most electronegative centre.

Interestingly, the thioketone group does not fit the EA/electronegativity trend, its positive EA being much higher than those of the other C=X groups. This finding is consistent with previous ETS and theoretical evidence of the role played by π*/S3d mixing in the stabilisation of Π anion states.

The C=S group, which also has the lowest IE (associated with the mainly sulphur lone pair σ orbital), therefore displays the largest electron-donor and electron-acceptor properties at one and the same time.

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