

ESCA STUDY OF HETEROCYCLIC COMPOUNDS: PENTATOMIC SATURATED DERIVATIVES.

by

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The ESCA method⁽¹⁾ has been applied to the study of some heterocyclic derivatives. As a first example we report the ESCA spectrum of tetrahydrothiophene, tetrahydrofurane, pyrrolidine and for comparison cyclopentane. The Fig.1 reports the kinetic energy spectrum of the various core electrons ejected from the above samples, solidified onto a cooled copper surface and bombarded with Mg K α radiation (1253.6 eV).

In the tetrahydrothiophene case the S_{2p}, S_{2s} and C_{1s} electron bands are shown. It is interesting to note the rather good resolution in our experimental conditions which allow us to observe clearly the spin-orbit splitting of the S_{2p} electrons. This splitting was found to be 1.15 ± 0.1 eV; such a figure is in agreement with previous values obtained for other sulphur compounds. In particular it is intermediate between those previously reported for thiophene in the gaseous⁽²⁾ and solid⁽³⁾ phases (1.25 and 1.0 eV respectively).

Again, in agreement with previous observations reported on other sulphur compounds⁽¹⁾, the S_{2s} electron band appears to be very broad.

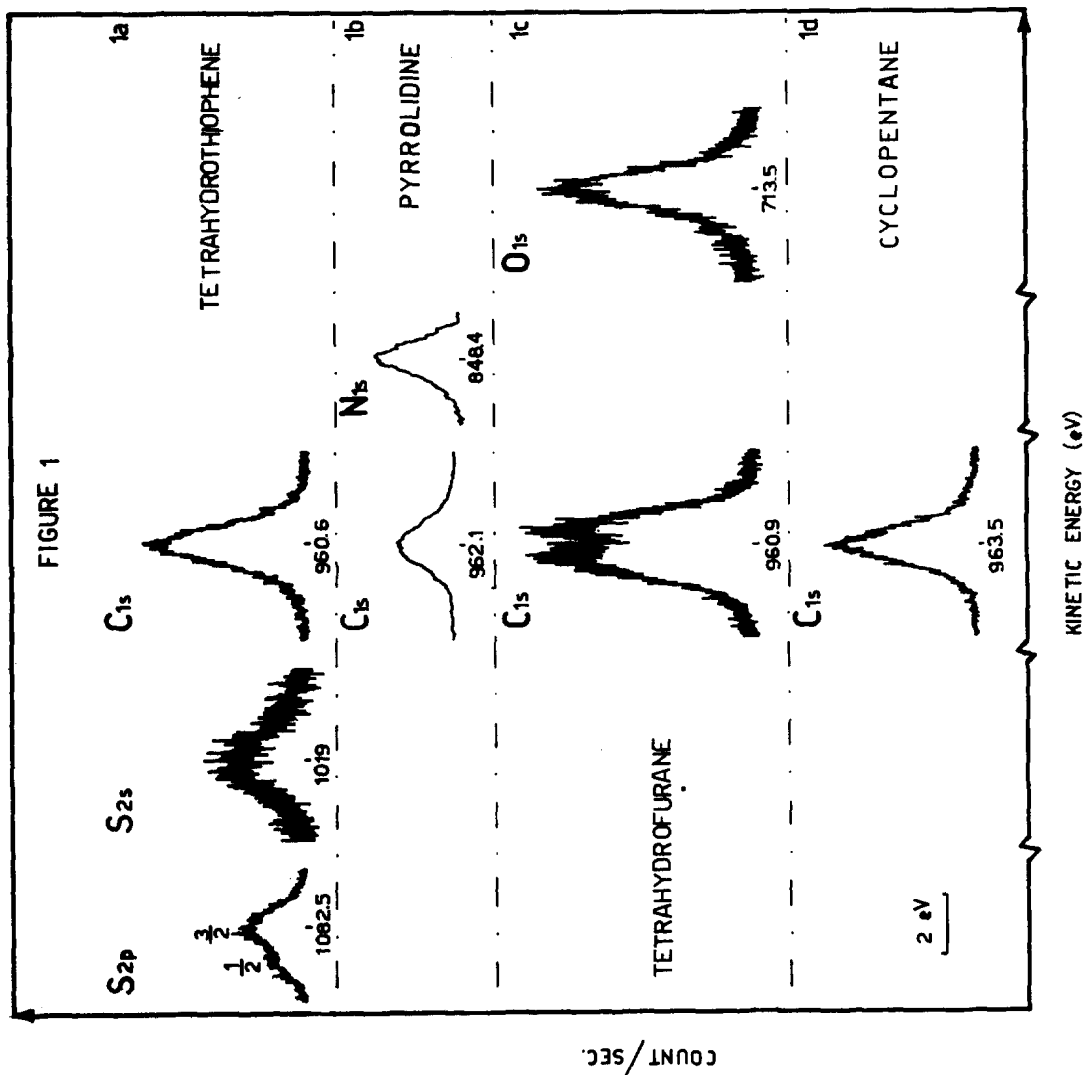


Fig. 1. C_{1s} photoelectron energy spectra of: a) tetrahydrothiophene; b) pyrrolidine; c) tetrahydrofuran; d) cyclopentane. The photoelectron peaks of the corresponding heteroatoms are also shown. The spectra were obtained by using an AEI E5 100 Electron Spectrometer. The energy scale is uncorrected.

As far as the C_{1s} electron band of tetrahydrothiophene is concerned, one can see that it is apparently unique so as in pyrrolidine and cyclopentane: by contrast, the same peak is clearly split into two components in the tetrahydrofurane.

Siegbahn and his coworkers have shown that there is a linear correlation between charge density on an atom and the ionization energy (or Binding Energy B.E.) of its inner electrons⁽⁴⁾. So that, the C_{1s} electron spectrum of tetrahydrofurane may be interpreted as due to C_{1s} electrons coming from the two different positions of the ring (2(5) and 3(4) respectively).

The difference in the B.E.'s of these electrons should be mainly due to the electronegativity effect of the oxygen atom which should lower the charge density on the 2(5) position more than in the 3(4) one. This suggests that we should assign the peak at lower kinetic energy E_k (higher B.E.) of the C_{1s} doublet to electrons coming from the 2(5) carbon atoms. The 1:1 intensity ratio of the two components supports the above interpretation. On the other hand, the energy separation of the two components of the band can be considered as a measure of the difference in charge density on the two kinds of tetrahydrofurane carbon atoms.

Following the above line, since the electronegativity of sulphur and nitrogen is lower than that of oxygen, the C_{1s} electron band of tetrahydrothiophene and pyrrolidine can be considered as due to two contributions which are unresolved in the present experimental conditions: the fact that both tetrahydrothiophene and pyrrolidine show a broader C_{1s} band than that of cyclopentane where all the atoms are equivalent, support this hypothesis.

These broad bands can be deconvoluted, as is generally done in similar cases⁽⁴⁾, by using the shape and width of the C_{1s} band of cyclopentane. This gives a separation of 0.65 ± 0.1 and 0.3 ± 0.1 eV between the 2(5) and 3(4) carbon atoms of pyrrolidine and tetrahydrothiophene respectively. These values may be compared to that of 1.3 ± 0.1 eV for the two kinds of tetrahydrofurane carbon atoms. This shows that the heteroatom does appreciably influence the core electrons and that this influence is mainly connected to the electronegativity of the heteroatom itself. This finding is in agreement with previous data reported for analogous compounds. In particular it is interesting to note that the C_{1s} band of both diethylether and ethanol show two components separated by 1.4 eV⁽⁵⁾. In the case of ethylamine, a deconvolution of the observed C_{1s} band gave⁽⁵⁾ a separation between the two unresolved components of about 0.7 eV.

Further work is in progress in this Laboratory in order to make a consistent comparison of the B.E.'s relative to the compounds here investigated with those of the corresponding aromatics (2,3).

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