Molecular Core Binding Energies; Carbon and Nitrogen 1*s* Levels for Adenine

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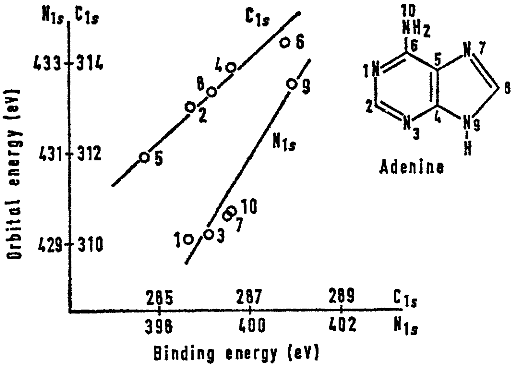
Summary The *X*-ray photoelectron spectra of the carbon and nitrogen 1*s* levels in adenine have been measured; the results are discussed in terms of the orbital energies in the neutral molecule.

X-RAY photoelectron spectroscopy provides an extremely powerful tool for investigating the electronic structure of molecules. In this and the following communication we present the results of an investigation of the molecular core binding energies for the nucleic acid bases adenine, cytosine, and thymine. These molecules form a particularly suitable series for investigation since they possess carbon and nitrogen atoms in widely differing electronic environments, they are of considerable chemical and biochemical interest and they represent some of the largest molecules for which the results of nonempirical all-electron quantum-mechanical calculations are available.[1] In this communication we present the results for adenine. The spectra which were excited using characteristic Al-K_α radiation, were measured with the prototype of the A.E.I. Scientific Apparatus Ltd. ES 100 spectrometer. Binding energies have been corrected for the work function of the spectrometer, but not charging of the sample, which was studied as a thin film on a cooled probe.

The carbon and nitrogen 1*s* molecular core binding energies for adenine (Figure) are shown in the Table.

A striking feature is the substantial overall shifts, spanning 3·1 ev for the C_{1s} levels and 2·3 ev for the N_{1s} levels.

Recently the results of nonempirical calculations with a small contracted gaussian basis set have become available[1] and this work forms the basis for a theoretical discussion of these results as we have outlined in the previous communication.[2] It is implicit in this approach that a linear relationship should exist between the measured binding energies and the orbital energies of the neutral molecule, and this certainly represents a stringent test of the theory. The Figure shows a plot of orbital energies against binding energies for the carbon and nitrogen 1*s* levels. Considering the limit basis set and the approximations inherent in this approach the correlations are quite promising. Particularly striking is the way the grouping of N_{1s} orbitals is reproduced, four very close together and one at high binding energy. The different proportionality constants for the two correlations may well arise from the limitations of the basis set. From the eigenfunctions it is now possible to assign particular energy levels to atoms in the molecule, since the orbitals are essentially localized. The assignment is shown in the Table, together with the gross atomic populations derived from a Mulliken population analysis. Whilst for the carbon 1*s* levels the trend is for higher binding energy to be associated with lower gross atomic population, for nitrogen the picture is clearly very complicated and this emphasizes yet again the caution necessary in relating charge density to shift. It will be instructive to investigate the density contour maps close to the nucleus which will give a much better indication of the electronic environment in the immediate vicinity of each atom.



FIGURE

TABLE

Atom†	1*s* Binding energy (ev) (±0·3 ev)	Gross atomic population (net) (in millielectrons)
C-5	284·7	−003
C-2	285·7	+178
C-8	286·2	+155
C-4	286·6	+344
C-6	287·8	+405
N-1	398·6	−511
N-3	399·1	−501
N-7 }	399·5	−425
N-10 }	399·6	−811
N-9	400·9	−670

† We are indebted to Prof. A. Pullman for these results.

C-5, which is directly bonded to only one nitrogen atom, has the lowest binding energy and there is a considerable spread in energy for C-2, C-8, C-4, and C-6 all of which are directly bonded to two nitrogens. N-9 has the highest N_{1s} binding energy by a considerable margin, the other nitrogens having very similar N_{1s} levels. This would not have been predicted from a consideration of the charge densities.

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[1] B. Mely and A. Pullman, *Theor. chim. Acta*, 1969, **13**, 278.

[2] M. Barber and D. T. Clark, preceding communication.