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

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

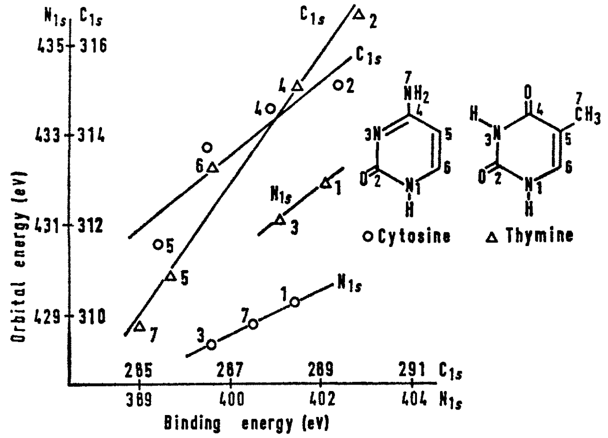
IN the preceding communications[1] we have described the *X*-ray photoelectron spectra of the carbon and nitrogen 1*s* levels for adenine and a simplified theoretical interpretation of these. We now present a similar discussion for cytosine and thymine (Figure). The results are shown in the Table. The energies cannot strictly be defined as absolute binding energies, since we have not corrected for the small shifts due to the electrical properties of the thin layer of irradiated material. Our experiments have shown that it is possible to vary the binding energies by several ev, depending on the sample characteristics, although this does not affect the relative energies for various levels within the sample.

The carbon 1*s* levels span a range of 4 ev for cytosine and almost 5 ev for thymine. The Figure shows a plot of calculated orbital energies[2] for the carbon and nitrogen 1*s* levels of the two molecules against measured binding energies. Separate correlations have been drawn for the two molecules since the charging effects may well be slightly different for the two samples. The differing slopes for the correlations in this and the previous communication most probably arise from the use of a limited basis set. The assignments of energy levels are given in the Table.

For these particular compounds the correlation between C_{1s} shifts and charge density is rather good. However, as with adenine, the correlation for the nitrogen 1*s* levels is poor.

For both molecules the carbonyl carbons have the highest C_{1s} binding energies and in thymine (where C-2 and C-4 are resolved) C-2, which is attached to *two* nitrogens, has the greater binding energy. This emphasizes the power of the technique in investigating the electronic structure of molecules. In both cases the carbons not attached to nitrogen or oxygen are the sites of lowest binding energy.

The nitrogen shifts also follow an interesting sequence, with the lactam nitrogens being at highest binding energies, and in thymine (where N-1 and N-3 are resolved) N-3, which is adjacent to *two* carbonyl groups, has the highest N_{1s} binding energy. For cytosine the binding energy for N-7 of the amino-group is higher than that of the ring nitrogen N-3, which would not have been predicted from simple considerations of charge density (Table).



FIGURE

TABLE

Molecule	Atom†	1*s* Binding energy (ev) (±0·3 ev)	Gross atomic population net (in millielectrons)
Cytosine	C-5	285·4	−480
	C-6	286·5	−13
	C-4	287·9	363
	C-2	289·4	637
	N-3	399·6	−461
	N-7	400·5	−719
	N-1	401·4	−597
Thymine	C-7	285·1	−820
	C-5	285·8	−144
	C-6	286·6	19
	C-4	288·5	562
	C-2	289·9	771
	N-3	401·1	−715
	N-1	402·1	−708

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[1] M. Barber, D. T. Clark, preceding communications.

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