Investigation of the Electronic Structure of 2-(Acetylamino)prop-2-enoic Acid (*N*-Acetyldehydroalanine) by He^{I} and He^{II} Photoelectron Spectroscopy

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He^{I} and He^{II} excited photoelectron spectra of *N*-acetyldehydroalanine (2-acetylaminoprop-2-enoic acid) are presented and discussed. Assignments are proposed by comparison with acetamide and acrylic acid and by analysis of the relative band intensities in the two spectra. The major perturbation with respect to the reference molecules arises from the interaction between the acetamido- and vinyl groups.

In the past few years photoelectron spectroscopy (p.e.s.) has been widely used to study the electronic structure of molecules of biological relevance. In particular, studies on amino-acids,[1] nucleic acids,[2] pyrimidines,[3] purines,[4] xanthines,[5] and piperazines [6] have been reported.

To date, p.e. investigations on amino-acids have been limited to saturated ones, wherein the C_α atom is sp^3-hybridized. However, many natural peptides,[7] which exhibit relevant biological activity, contain αβ-unsaturated residues, wherein C_α is sp^2-hybridized. The study of the conformational behaviour and of the electronic structure of these αβ-unsaturated residues is in progress in our laboratories. In previous papers we reported on the *X*-ray structure of *N*-acetyldehydroalanine [8] and theoretical conformational investigations on model compounds of unsaturated peptides.[9]

We discuss here the He^{I} and He^{II} excited p.e. spectra of the *N*-acetyl derivative of dehydroalanine, which is the simplest αβ-unsaturated amino-acid.

EXPERIMENTAL

Commercial *N*-acetyldehydroalanine (Ega Chemie) was sublimed prior to use. Spectra were run at 100 °C on a Perkin-Elmer PS-18 spectrometer modified by inclusion of a hollow cathode discharge lamp giving high photon flux at the He^{II} wavelength (Helectros Developments). Spectra were calibrated by reference to peaks due to admixed inert gases and to the He $1s^{-1}$ self-ionization.

RESULTS AND DISCUSSION

The He^{I} and He^{II} p.e. spectra of *N*-acetyldehydroalanine are shown in Figure 1. They appear better resolved than those of saturated amino-acids.[1] This certainly relates to the sp^2-nature of the C_α atom, since the presence of tetrahedrally hybridized atoms complicates the p.e. spectra to some extent.

For discussion purposes, the spectra are analysed in terms of three distinct spectral regions (8.5—10.5, 10.5—13, and 13—19 eV). In the first region two well resolved bands (labelled A and B in Figure 1) are present. In the next region the He^{I} spectrum shows two bands (D and E). Band D has a relevant shoulder (C) on its low ionization energy (IE) side. Under He^{II} radiation, the shoulder C increases in intensity compared with band D (Figure 1). Band E is accompanied by a vibrational progression (*ca.* 1 450 cm^{-1} interval). The third region includes at least three defined bands (G, M, N) and the shoulder F which appears on the low IE side of band G.

Our assignment of the spectrum is based on a correlation between the IEs measured in the molecule of interest and those of related simple compounds. Figure 2 shows such a correlation diagram: acetamide [10] and acrylic acid [11] are the reference compounds.

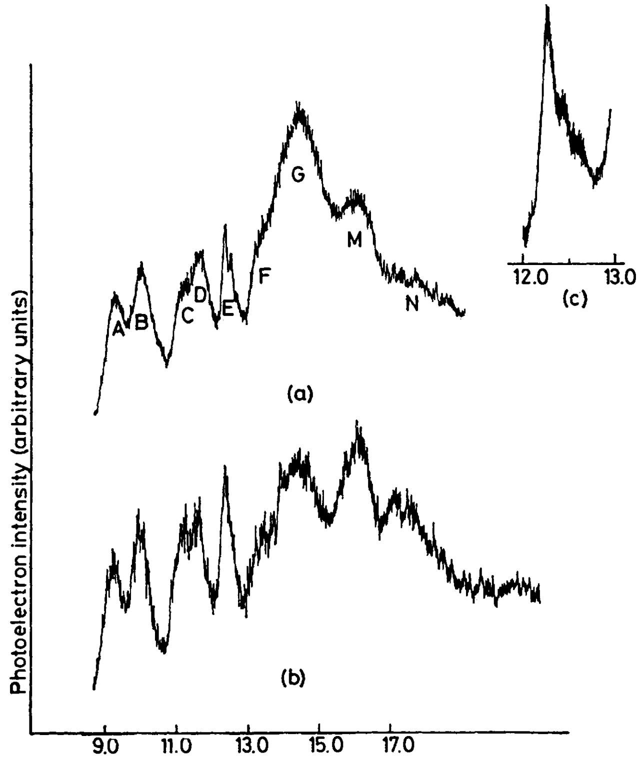

FIGURE 1 P.e. spectra of *N*-acetyldehydroalanine: (a) He^{I} spectrum; (b) He^{II} spectrum; (c) detail of band E (from He^{I} spectrum)

Throughout the following discussion we will assume that title compound is fully planar.† This situation

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† Adopting the standard [12] definitions for torsion angles of amino-acids and peptides, we have $\phi = \psi = \omega = 180°$.

prevails in the crystal state,[8] and according to previous conformational calculations[8] we feel confident that a planar conformation is maintained in the gas phase also.

Bands A and B certainly represent ionization from molecular orbitals (MOs) which are the counterparts of n_O and π_N MOs of acetamide,[10] *i.e.* the in-plane lone pair of the carbonyl oxygen and nitrogen out-of-plane lone pair, respectively. On the basis of simple qualitative MO arguments, it transpires that band A must be assigned to the π_N ionization, while band B relates to the n_O MO, a reversed order with respect to acetamide.[10] The interaction between the π_N level and the inner $\pi_{C=C}$ MO of the acrylic fragment is responsible for the low IE shift of the π_N ionization in the title compound (see Figure 2). This assignment implies a value for n_O ionization lying in the IE range usually found.[10] Furthermore, the same pattern has been found in other molecules containing the enamido-group (*e.g.* uracil[3] and xanthine[5]). The comparison with these planar and conformationally rigid molecules supports the hypothesis of a planar conformation for *N*-acetyldehydroalanine in the gas phase, at least as far as the ϕ torsion angle is concerned.

Measured vertical IEs values (eV) of *N*-acetyldehydroalanine and proposed assignments

Band	Vertical IE	Assignment
A	9.24	π_N
B	9.91	n_O
C	11.11	n_O'
D	11.58	$\pi_{C=C}$
E	12.26	π_{CO_2H}
F	13.40	σ_{CH}
G	14.34	σ_{CC}, $\pi_{C=O}$(amide)
M	15.83	$\pi_{C=O}$ (carboxy)
N	17.5	

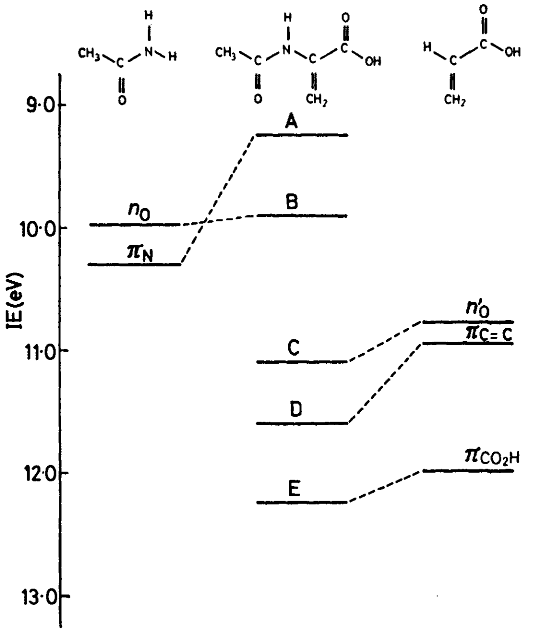

FIGURE 2 Correlation diagram of experimental ionization energies between acetamide,[10] *N*-acetyldehydroalanine, and acrylic acid.[11] Bands are labelled according to the Table

As for the second spectral region, bands C—E match the three lower ionizations present in the p.e. spectrum of acrylic acid.[11] They correspond (Figure 2) to ionizations from the in-plane lone pair of the carboxy oxygen (n_O'), from the $\pi_{C=C}$ bonding MO, and from the non-bonding antisymmetric π MO localized on the CO_2H group (π_{CO_2H}). The first two ionizations give rise to one ill resolved band in acrylic acid, while in the title compound shoulder C is clearly resolved. In line with the previously mentioned interaction between π_N and $\pi_{C=C}$ MOs, C and D are assigned to n_O' and $\pi_{C=C}$ MOs, respectively. Furthermore, under He^{II} radiation shoulder C undergoes a marked increase in intensity over band D (Figure 1). This behaviour reflects the increased photoionization cross-section[13] ratio $\sigma(O_{2p})/\sigma(C_{2p})$ at the He^{II} wavelength and confirms the proposed assignment. The remaining band E we take to represent ionization from the π_{CO_2H} MO: both its IE value and the energy difference (1.15 eV) from band C (*i.e.* $n_O' - \pi_{CO_2H}$ separation) are within the range usually found in carboxylic acids.[10]

Finally, we consider the last spectral region where ionizations from π-bonding MOs and from MOs localized in the molecular σ-framework are expected. On the basis of earlier work[11] it appears that the broad band G together with its shoulder F represent ionizations from σ_{CH} and σ_{CC} MOs. The relative lowering of the intensities of these bands in the He^{II} spectrum presumably reflects the H_{1s} contribution to these MOs, the atomic cross-section[13] for the H_{1s} atomic orbital being rather low at the He^{II} wavelength.

The marked increase in relative intensity of band M in the He^{II} spectrum is a clear indication of the dominant O_{2p} contribution to the MO which is responsible for this ionization. Thus, band M is likely to correspond to ionization from the π-bonding MO localized on the carboxy-group. Similar values of the IE have been found in acrylic acid[11] as well as in aliphatic carboxylic acids.[10] Within our proposed assignments we have left the π-bonding MO localized on the acetamido-group unassigned. Generally, in amides[14] this ionization occurs at *ca.* 1 eV lower IE than in the corresponding acids. Thus, we feel confident in assuming that the ionization in question is hidden beneath the broad band G.

Conclusions.—By reference to acetamide and acrylic acid, the electronic structure of *N*-acetyldehydroalanine can be satisfactorily described in terms of a major perturbation due to interaction between the $\pi_{C=C}$ MO and the π_N MO of the acetamido-fragment. There is no evidence of strong perturbation on the carboxy-group MOs. On the other hand, mutually independent barriers around ϕ and ψ torsion angles proved suitable[8,9] for describing the conformational behaviour of *N*-acetyldehydroalanine and related peptide residues. This fact seems to be in tune with our interpretation of the p.e. results.

We also performed extended basis-set *ab-initio* calculations on the molecule of interest but, assuming Koopmans' approximation, we achieved no satisfactory fitting with the measured p.e. spectrum. It is our opinion that this is a common feature of molecules containing $\alpha\beta$-unsaturated carbonyl groups and we will discuss this aspect in a forthcoming paper.[15]

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