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Photoelectron spectroscopy of lactams

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ABSTRACT: He I and He II photoelectron spectra (UPS) of several lactams were measured and analyzed on the basis of empirical arguments and *ab initio* calculations. The electronic and molecular structure of the amide group is discussed on the basis of experimental and theoretical results. Relative basicities of nitrogen centre(s) are also discussed within the framework of inductive and resonance effects. Copyright © 1999 John Wiley & Sons, Ltd.

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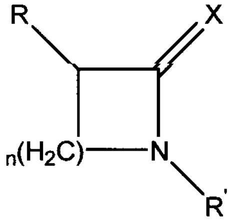
INTRODUCTION

The amide group in lactams can assume a variety of interesting molecular and electronic configurations which are dependent on prevailing orbital and steric interactions. We have studied a series of lactams that can be described by the general formula



$R = H, NMe_2, NH_2$
$R' = H, Me, CH_3CO$
$X = O, S$

The amide group is characterized by the principal geometric parameter Φ, which is the dihedral angle between the N2p (lone pair) axis and the NCX plane. Changes in substitution will influence Φ and thus the electronic distribution within the amide group. The electronic structure (distribution) can be studied by a combination of UV photoelectron spectroscopy (UPS) and semi-empirical MO calculations. Rademacher and co-workers[1–3] investigated the effects of ring size (n) and substituents (R′) on the structure of the amide group by this approach. Their main conclusions, which are relevant to the present work, are summarized as follows:

1. The two orbitals localized on amide group, which have the lowest ionization energies (*IE*) are π_N (nitrogen lone pair) and n_O (oxygen lone pair) with $IE(\pi_N) < IE(n_O)$.
2. The absolute values of ionization energies IE_1 and IE_2 and their difference ΔIE can be used to probe the molecular structure of the amide group.
3. An increase in the ring size leads to broadening of the first two bands, to an inductive shift of HOMO and HOMO-1 ionizations towards lower *IE* and to a decrease in ΔIE.

The analysis of Rademacher and co-workers[1–3] was based on band shapes, MNDO calculations and (sometimes) poorly resolved vibrational fine structure. In the spectra of many lactams the first two bands overlap strongly, thus making MNDO results (based on Koopmans approximation) unreliable. We have therefore measured all spectra with different photon energies (He I/He II) in an attempt to arrive at definitive assignments. Furthermore, we have studied the range of lactams whose electronic structures show greater variations than those investigated by Rademacher and co-workers.

EXPERIMENTAL AND THEORETICAL METHODS

The He I and He II spectra were recorded on a Leybold–Heraeus UPG-200 spectrometer with a spectral resolution of 20 meV, measured as the FWHM of $Ar^{+2}P_{3/2}$ and $^2P_{1/2}$ calibration lines. Elevated sample temperatures (60–130 °C) were used during measurements of less volatile compounds in order to obtain sufficiently high vapor pressures. The compounds were purchased from Sigma-Aldrich with a purity better than 95%. *Ab initio* calculations at the $6–31 + G^*$ level were performed with the Spartan set of programs.[4] The aims of the calculations were to deduce the angle Φ, to assess whether the measured spectra refer to the mixture of

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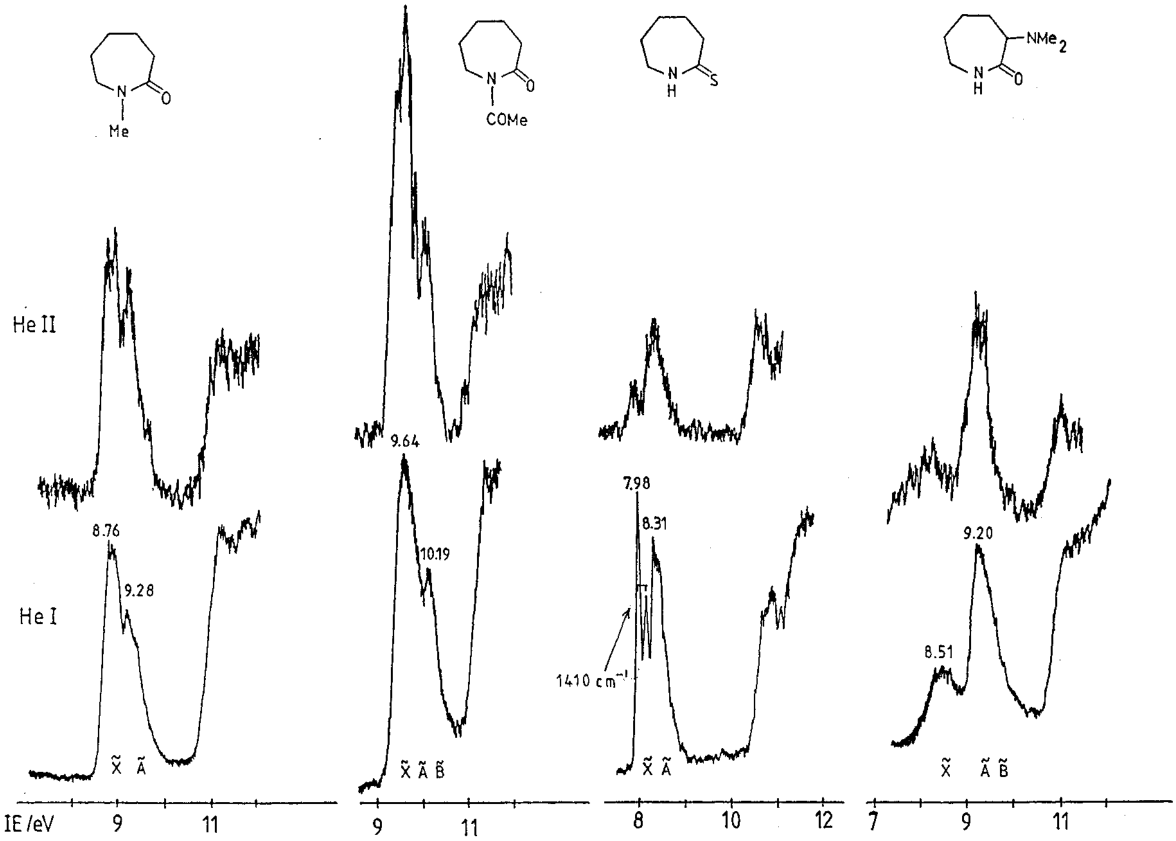

Figure 1. He I/He II photoelectron spectra of lactams

conformers in the gas phase and to help in the spectral assignment (using Koopmans approximation). A full conformational space search was conducted with the Spartan program. The results showed that at the temperatures of the experiment (assuming a Boltzmann distribution), the most stable conformers were present in excess of 95%. The estimates of the angle Φ hence refer to the most stable conformers only.

RESULTS AND DISCUSSION

He I and He II photoelectron spectra of the lactams studied are shown in Figs 1 and 2. In addition, we measured He I/He II spectra of δ-valerolactam, 2-azacyclooctanone, 2-azacyclononanone and ε-caprolactam. The additional spectra are in full agreement with He I spectra published by Rademacher and co-workers[1–3] and are therefore not reproduced here. The purpose of re-measuring them with different photon energies was to check the assignments proposed earlier[1–3] for π_N and n_O ionizations. However, strong band overlap prevented the observation of significant changes on going from He I to He II radiation. Only in *N*-methylcaprolactam (Fig. 1) did the relative intensities of the *X* and *A* bands change, suggesting that $IE(\pi_N) < IE(n_O)$. This conclusion follows

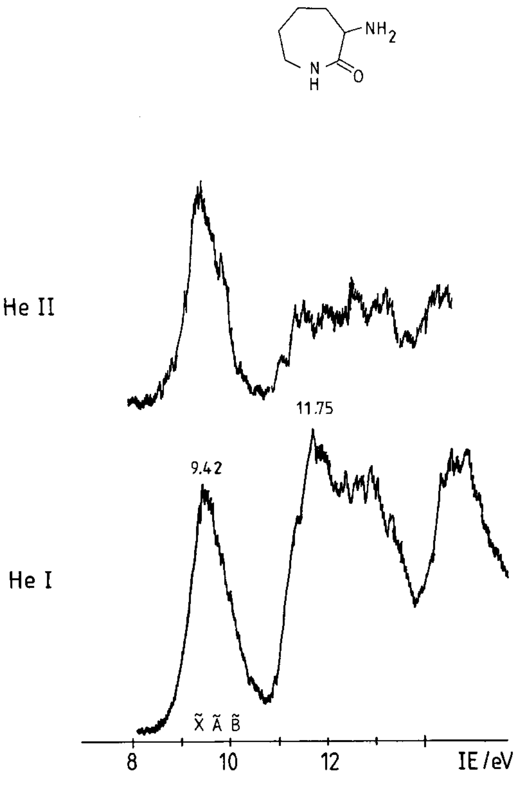

Figure 2. He I/He II photoelectron spectra of the lactam shown

Table 1. Vertical ionization energies (*IE*) and *ab initio* orbital energies (ε) for caprolactams

Derivative	Band	ε (eV)	*IE* (eV)[a]	Assignment	Φ (°)
N-Methyl	*X*, *A*	9.85, 10.53	8.76, 9.28	π_N, n_O	86.8
N-Acetyl	*X*, *A*, *B*	10.78	(9.64)	n_O(lactam)	92.15
		11.42	(9.64)	n_O(acetyl)	
		11.78	10.19	π_N	
Thiocaprolactam	*X*, *A*	8.19, 8.39	7.98, 8.31	n_S, π_N	88.2
α-Dimethylamino	*X*, *A*, *B*	9.43	8.51	π_{Nme_2}	93
		10.35	(9.20)	π_N	
		11.03	(9.20)	n_O	
α-Amino	*X*, *A*, *B*	10.20	(9.42)	π_{NH_2}	92.8
		10.45	(9.42)	π_N	
		11.19	(9.42)	n_O	

[a] The parentheses designate unresolved bands.

from the consideration of atomic photoionization cross-sections[5] for N2p and O2p orbitals under He I and He II radiation. The He II/He I O2p cross-section ratio is 0.64 compared with the same ratio for N2p, which is 0.45. This indicates that ionization from an orbital with higher O2p character should give rise to an increase in the relative band intensity, which is exactly what was observed for the 9.28 eV band. This argument supports Treschanke and Rademacher's original assignment[1].

The assignments and *IE* values are summarized in Table 1. The rationale behind them is interesting and merits further discussion. 'Koopmans analysis' (i.e. fixed photon energy measurements combined with MO calculations) is not adequate for assignment purposes if bands are closer in *IE* than 0.5 eV.

N-Acetylcaprolactam

The comparison of the spectrum of *N*-acetylcaprolactam with the UPS of acetone[6] suggests the presence of three ionizations in the 9–11 eV region. The He I/He II intensity changes indicate that the 10.19 eV band belongs to π_N ionization because of the relative intensity decrease. The 9.64 eV band can then be attributed to ionizations from oxygen lone pairs (n_O) localized on acetyl and lactam keto groups. We may expect *N*-acetylcaprolactam to have a much lower Lewis basicity than the unsubstituted lactam. The observation that $IE(\pi_N) > IE(n_O)$ is unusual for lactams.[1–3]

It can be explained by strong conjugation (delocalization) taking place within π_{CO}–π_N–π_{CO} moiety. The delocalization introduces C2p and O2p character into the π_N orbital; the latter contribution will cause π_N level stabilization.

Thiocaprolactam

The replacement of oxygen in ε-caprolactam with sulfur causes an inductive shift of the n_S level towards lower *IE* and reverses the π_N–n_S order, making $IE(\pi_N) > IE(n_S)$. The assignment of π_N and n_S ionizations is again made straightforward by considering the He II/He I intensity variations. The S3p and N2p cross-section ratios at He II/He I energies are 0.14 and 0.45, respectively, which suggests a strong decrease in relative intensity for the n_S band. The contour and vibrational fine structure (1410 cm^{-1}; C-S stretch) of the n_S band also indicate that the sulfur lone pair is more localized and a better nucleophilic centre than the carbonyl oxygen.

α-Aminocaprolactam

The comparison of the spectrum in Fig. 2 with the spectra of methylamines[6] indicates that the 9.42 eV band contains three unresolved ionizations. Once again, 'Koopmans analysis' is not useful for determining the relative ordering of levels. The He I/He II measurements suggest that n_O has the highest ionization energy (note the shoulder appearing in the He II spectrum), while lactam and amine nitrogens have similar energies. This situation can be contrasted with the α-dimethylamino derivative, where the nitrogen lone pair energies for lactam and amine groups are very different.

α-Dimethylaminocaprolactam

Comparison of the spectra of this derivative with those of methylamines[6] suggests the assignment listed in Table 1. The π_{NMe_2} band at 8.51 eV is very broad, which is indicative of hyperconjugative interactions. The possible interactions could take place either between the nitrogen lone pair (π_N) and methyl groups or between π_N and the oxygen lone pair (n_O). The former case appears to be more plausible because of the lack of enhancement in π_{NMe_2} intensity on going from He I to He II radiation. Such an enhancement would be expected if the orbital in question were to acquire O2p character via hyperconjugation. As mentioned previously, the amine nitrogen appears to be more basic than the lactam nitrogen.

Substituent effects

R and R′ substituents may induce changes in the extent of π_N–π_{CO} conjugation. Our discussion of possible changes will be based on UPS data rather than MO calculations and thus be independent of MO algorithms and Koopmans approximation. The π_N and n_O ionization energies in —NR$_2$ (R = H, Me) substituted lactams are close to 9.19 and 9.52 eV, respectively, in the parent lactam.[1] The R substitution exerts only a small inductive perturbation on the amide group. This is in line with stereochemical considerations which show that the —NR$_2$ nitrogen is not positioned favourably for N2p–N2p interaction with the amide group. On the other hand, R′ substitution strongly affects the lactam group as can be seen from the comparison of the spectra of *N*-acetyl and *N*-methyl derivatives with that of the unsubstituted lactam. The relative significance of inductive and conjugative effects of R′ substituents can be discerned from ΔIE and the absolute *IE* values. The inductive effect will not influence ΔIE value whereas conjugative effects will change both ΔIE and *IE* values. After taking these arguments into consideration, one may conclude that methyl and acetyl substituents affect the amide group via both inductive and conjugative interactions (Fig. 1).

The replacement of the heteroatom in a C═X group causes inductive (changed *IE*) and conjugative perturbations (changes in the bandshapes of π_N and n_O ionizations). This can be seen clearly in the spectrum of thiocaprolactam, where the *X* and *A* bands have very different shapes and *IE* compared with the parent lactam.[1]

The angle Φ was found to deviate only slightly from 90° (Table 1), which is the most favourable configuration for π_N–π_{CO} interaction and delocalization.

CONCLUSION

We have analyzed the electronic structure of lactams using variable photon energy UPS measurements. One of the properties which may be predicted from the measurements are relative gas phase basicities (*GB*) of the title compounds. The feasibility of such a prediction can be tested by correlating π_N ionization energy and pK_b constants. *GB* values for lactams have not been determined experimentally so we used the best available measurements performed in solution.[7] The comparison (Table 2) indicates that an increase in ring size generates more basic compounds. Furthermore, *N*-methyl substitution also leads to an increase in basicity. The *IE*–pK_b correlation shows a monotonous variation except for δ-valerolactam, where the measured pK_b appears too high. Table 2 also suggests that the *IE*–pK_b correlation is applicable only within the same group, i.e. one cannot compare the basicities of substituted and unsubstituted lactams directly. This is probably due to thermodynamic contributions arising from different solvation effects for substituted and unsubstituted molecules.

Table 2. Comparison of nitrogen lone pair *IE* (eV) (π_N)[1] and basicity constants (pK_b, 25 °C)[7]

n (ring size)	π_N	pK_b
4	9.78	−0.96
5	9.37	−0.65
6	9.30	−0.18
7	9.19	−0.46
8	9.19	−0.38
9	9.12	−0.18
5 (*N*-Me)	9.17	−0.75

On the basis of UPS data we can predict that α-dimethylaminolactam will be the most basic and the *N*-acetyl derivative the least basic amongst the compounds studied. Also, a thiolactam will be more basic than its lactam analogue. The predictions refer to *GB* and are therefore applicable to substituted and unsubstituted derivatives.

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