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Ultraviolet Photoelectron Spectroscopic Study of Highly Flexible Molecules: Aza Macrocycles

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Introduction

Recent studies of nitrogen macrocycles emphasized several reasons why such compounds are of interest to a wider circle of chemists. The first reason is related to their high degree of conformational flexibility which permits the observation of unusual conformations where bulky substituents like *tert*-butyl groups[1] eclipse both axial and equatorial exocyclic N−CH$_2$ bonds.[1] The second interesting property of aza macrocycles concerns formation of charge-transfer complexes with electron acceptors (e.g. iodine) in solution and in the solid state.[2] Finally, their electron-donating ability is one of the factors influencing relative stabilities and rates of formation of complexes formed between these ligands and various metal ions.[3] The generalizations regarding macrocyclic complexation behavior must, however, take into account ligand−solvent interactions.[4] Although the macrocyclic effect had been known for a long time some of its details are still unclear. The purpose of this work was to help unravel the contribution of electronic structure effects in complex formation and to obtain conformational information about the free macrocyclic ligand molecules. The experimental conformational studies of such highly flexible molecules were, until now, confined to solid state (X-ray diffraction) and liquid phase (NMR). In the solid state usually only a single conformer exists with crystal packing constraints selecting the most suitable one. In the liquid state, several conformers may be present, but solvent−solute interactions will again modify the conformer distribution. The gas-phase ultraviolet photoelectron spectroscopy (UPS) probes the electronic structure directly and can also provide some conformational information.

Experimental and Computational Methods

The sample compounds (>97% purity) were obtained from Aldrich and used without further purification after checking their melting and boiling points. Spectra were recorded with modified Perkin-Elmer PS16/18 photoelectron spectrometers. For molecules **1** and **2** which gave sufficient vapor pressure at room temperature, spectra were recorded using a spectrometer with a fixed analyzer pass energy of 2 eV and with Ar$^+$ $^2P_{3/2}$ resolution of <25 meV. Molecules **3**−**6** required an instrument with a heated ionization chamber (temperatures 30−1500 °C). Spectra were recorded by scanning the analyzer pass energy. Ar$^+$ $^2P_{3/2}$ resolution with this instrument was around 30 meV. Ionization energies were calibrated with respect to the known features in Ar and N$_2$O spectra. No signs of decomposition (e.g. hydrolysis) of the sample compounds could be detected in the spectra.

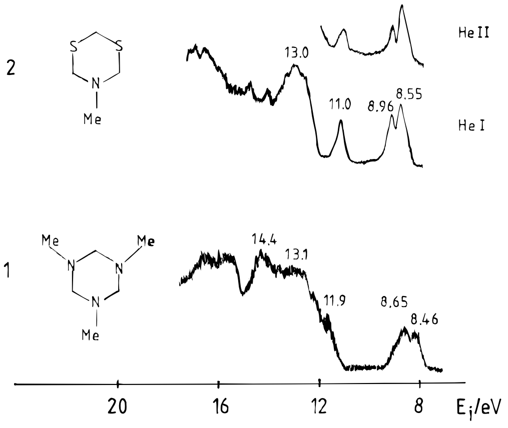

Figure 1. Photoelectron spectra of macrocycles with three heteroatoms.

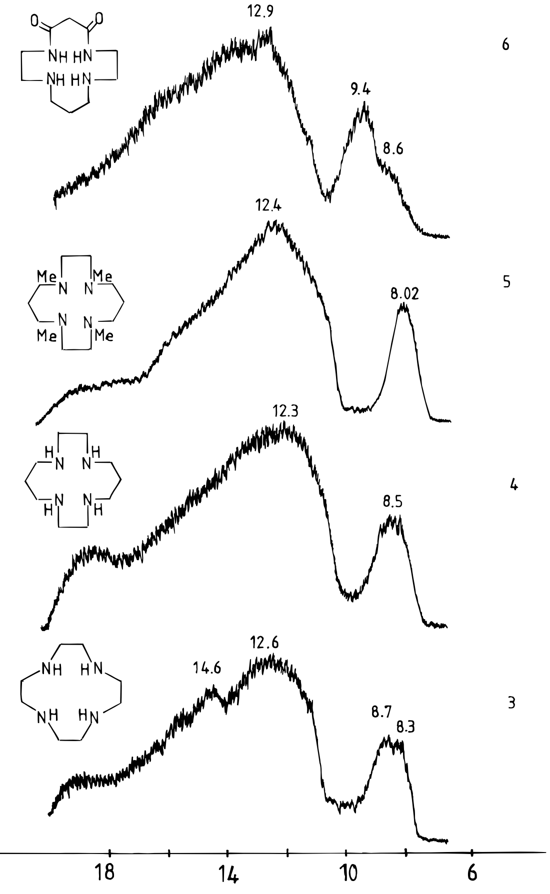

Figure 2. Photoelectron spectra of tetraaza macrocycles.

Molecular structures were initially constructed and minimized with SPARTAN[5] molecular mechanics (MM) module using SYBYL force field. The same force field was used to perform full conformational space search. The molecular structure of each conformer was then optimized with the semiempirical AM1 method.

Results and Discussion

The He I photoelectron spectra (UPS) of aza macrocycles **1**−**6** are shown in Figures 1 and 2. The most interesting regions of the spectra are those at E_i < 10 eV where bands corresponding to heteroatom lone pair

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Table 1. Ionization Energies/(E_i, eV) and Assignments of UPS Spectra of Macrocycles

molecule	E_i	assignment[a,b]
1	8.46	n_N
	8.65	n_N, n_N
2	8.55	n_S^-, n_N
	8.96	n_S^+
	11.0	σ_{CS}
3	8.3, 8.7	4 n_N
4	8.5	4 n_N
5	8.02	4 n_N
6	8.6	4 n_N
	9.4	n_O^-, n_O^+

[a] n_N and n_o represent nitrogen lone pairs and oxygen lone pairs of the carbonyl groups, respectively. [b] n_S^- and n_S^+ are in-phase and out-of-phase LCAO of S3p.

ionizations were observed. The band assignments are straightforward and are based on the results of AM1 calculations[5] and (in case of molecules **2** and **6**) comparisons with UPS of cyclic 1,3-diketones[6] and 1,3-dithiane.[7] The assignment of the UPS spectra of **2** also relies on the He I/He II intensity variation (Figure 1). The spectrum of **2** shows that the relative intensities of bands at 8.96 eV and 11.0 eV decrease on going to He II excitation. One can refer to relative atomic photoionization cross-sections[8] which show that the He II/He I cross-section ratios for N2p and S3p are 0.449 and 0.139, respectively. The two aforementioned bands can thus be assigned to ionizations of orbitals (n_S^+, n_S^-) with significant S3p character (Table 1). The ring heteroatoms' np orbitals (lone pairs) may be expected to interact via through-bond (TB) or through-space (TS) mechanisms. While both mechanisms may be active, the former is relatively less conformation sensitive than the latter, as was demonstrated previously.[9]

TS effects are important part of a UPS probe into molecular conformations, bearing in mind that UPS is not a method of choice, but rather of necessity.

The comparison of the UPS of tetraaza, tetraoxo-,[10] and tetrathia-[11] cyclododecanes and cyclotetradecanes suggests that aza and thia macrocycles have similar Lewis basicity, which is however greater than that of oxo analogues. Different stabilities of metal complexes of aza and thia ligands must then be attributed to steric (ligand ring and metal ion sizes) and/or thermodynamic factors (enthalpy of formation). The bandwidths of heteroatom lone pair ionizations can provide insight into the conformations of these highly flexible molecules. The larger the splitting (bandwidth), the greater the TS interactions and hence the closer the heteroatoms will be in space. UPS results indicate that endodentate conformers have larger Boltzmann populations in oxo and aza than in the corresponding thia macrocycles.

Measured full-width-half-maxima (FWHM) of lowest ionization energy bands in **4** and **5** were 1.0 and 1.3 eV, respectively. The effect was not due to varying instrumental resolution, since the resolution was checked prior to recording of each spectrum. The ionization energy of the tetramethyl derivative **5** is lower than **4** because of the increased inductive electron supply to the nitrogen atoms. The smaller bandwidth of **5** (compared to **4**) indicates that the average N−N distance is longer in **5**, leading to smaller TS interactions.

This assumption was tested by MM conformational search and AM1 calculations. The MM results indicated that the average N−N distances in **5** and **4** are 0.292 and 0.344 nm, respectively. The averages were calculated for 10 (out of 50) most abundant conformers whose weightage (based on MM energies) was >3% with total energy span of 26 kJ mol^{-1}. The energy span of four nitrogen lone pairs in **4** and **5** was then calculated by AM1 method for each of 10 MM conformers. The average lone pair ranges were found to be 0.697 and 0.546 eV for **4** and **5**, respectively. This result seems to support our original assertion that different bandwidths observed are the result of different conformational distribution and N−N distances.

The rationale for different energy spans is related to the presence of Me substituents whose steric requirements may disfavor certain conformers. Most studies of large flexible molecules rely on MM or other molecular simulation techniques to unravel the conformer population, so this is one of the few experimental results available which provides some insight into the conformation of large macrocyclic rings in the gas phase. The goal of detailed UPS conformational analysis in molecules this complex is of course elusive, but ironically, the UPS method provides information which gas-phase electron diffraction and microwave spectroscopy could not.

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