



Electronic structure and tautomerism of aryl ketones



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ABSTRACT

The electronic structures of several aryl ketones (AK) and their α -halo derivatives have been studied by UV photoelectron spectroscopy (UPS). The relative stabilities of keto–enol tautomers have been determined using high-level ab initio calculations and the results were used in the analysis of UPS spectra. The main features of electronic structure and tautomerism of the AK derivatives are discussed.

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1. Introduction

Aryl ketones (AK) are compounds with important applications [1–3]. They have been used as photosensitizers due to their high triplet state energies, very efficient inter-system crossing (ISC) from singlet to the triplet states and long triplet state lifetimes. The presence of heavy atoms (e.g. halogens in our AK compounds) can significantly enhance the efficiency of ISC. AK have also found uses as photoinitiators (by generating radical intermediates) and as UV light blockers in cosmetic or plastic products. AK molecules are examples of photo-labile molecules which can be used in chemical biology for making “caged compounds” or in organic synthesis as photo-removable protection groups. The electronic structure of AK (especially characteristics of the HOMO) can be expected to play a significant role in governing their photochemical properties.

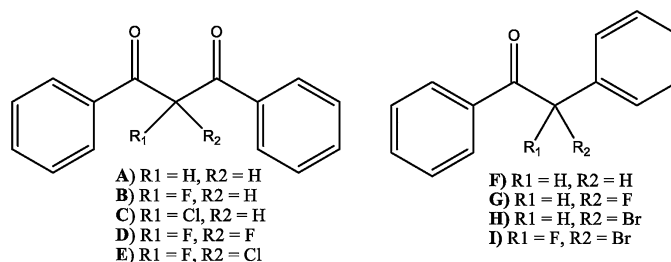
This is why we have performed the electronic structure study of several AK by using UV photoelectron spectroscopy (UPS) and related the studied electronic structures to the previously investigated molecular conformations, tautomerism and intramolecular hydrogen bonding (Scheme 1).

The UPS method gives an accurate description of the valence electronic structure of the free molecule so the comparison with

molecular structure in the solid state can be useful for gauging the influence of crystal packing forces on molecular geometries.

2. Experimental and computational methods

The samples of the compounds used were prepared and their purity checked according to the reported procedures [4]. The Hel/HeII photoelectron spectra (UPS) were recorded on the Vacuum Generators UV-G3 spectrometer and calibrated with small amounts of Xe gas which was added to the sample flow. The spectral resolution in Hel and HeII spectra was 20 meV and 60 meV, respectively when measured as FWHM of the $3p^{-1}2P_{3/2}Ar^+ \leftarrow Ar(1S_0)$ line. The samples were studied with the inlet probe temperatures between 100 and 160 °C. The spectra obtained were reproducible and were measured at constant vapour pressure. No signs of decomposition were detected. Decomposition is usually demonstrated by the



Scheme 1. Structures of AK studied.

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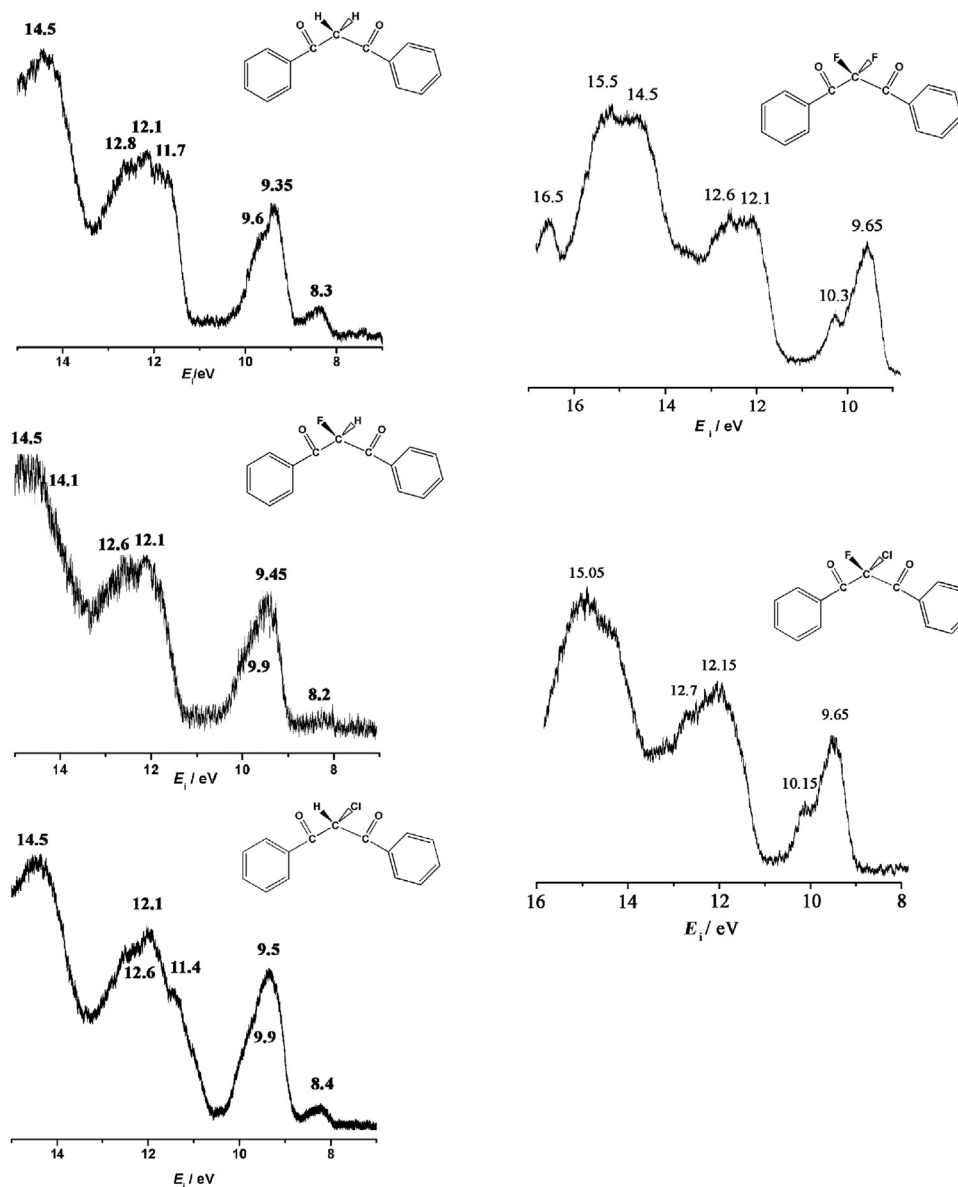


Fig. 1. UV photoelectron spectra of 1,3-diphenyl-1,3-propanediones.

appearance of sharp intense peaks which are due to the presence of small molecules/decomposition products in the spectrometer's ionization chamber.

The quantum chemical calculations were performed with the Gaussian 09 program [5] and included full geometry optimization of neutral molecules at B3LYP/6-31G* level. The vibrational analysis confirmed that the resulting geometry was the true minimum (no imaginary frequencies). Subsequently, the optimized DFT geometry was used as the input into the single point calculation using the outer-valence Green's function (OVGF) method and the 6-311G(d,p) basis set [6]. This method obviates the need for using Koopmans approximation and provides vertical ionization energies with typical deviation of 0.3–0.5 eV (depending on the size of the basis set) from the experimental values. The calculated geometries agree well (± 0.005 Å for bond lengths, ± 0.1 deg for bond angles) with the molecular geometries of those compounds whose structures have been determined by X-ray diffraction [7–9]. Intermolecular forces in the condensed phase are expected to affect molecular geometry, but they mainly affect molecular conformations (dihedral angles) being too weak to alter chemical bonds/bond

angles. The total electronic energy for each molecule was computed using the high-level composite G3MP2B3 method [10] which has root-mean-square deviation of 4 kJ/mol. The method includes full geometry optimization at the B3LYP/6-31G(d) level followed by the single point QCISD type calculations. The total electron energy was used to determine relative free energies of the possible tautomers.

3. Results and discussion

The HeI and HeII photoelectron spectra of AK are shown in Figs. 1 and 2. The spectral assignments are summarized in Table 1 and are based on OVGF calculations, the HeI/HeII intensity variations and comparison with the UPS of related molecules [11–15]. The ionization energies of related molecules are given in Table 1. The assignments of the spectra of some AK were also supported by changes in relative band intensities on going from HeI to HeII radiation. The calculated HeII/HeI atomic photoionization cross-section ratios for C2p, O2p and Br4p are 0.31, 0.64 and 0.06, respectively [16]. These known ratios allowed us to identify ionizations

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