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Computational study on the ionization energies of benzyl azide and its methyl derivatives

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ABSTRACT

Ionization energies of benzyl azide (BA), $C_6H_5CH_2N_3$, its methyl derivatives, 2-, 3- and 4-methyl benzyl azide and (1-azidoethyl)benzene (2-, 3- and 4-MBA and 1-AEB), $(CH_3)C_6H_4CH_2N_3$, have been calculated with several basis sets, with Møller–Plesset and Hartree–Fock methods. The data are compared to the ionizations energies obtained from HeI photoelectron spectroscopy (UVPES) experiments, in order to support the correct assignment of the bands. The nature and character of the molecular orbitals are also discussed.

1. Introduction

During the past three decades, several compounds containing the azido group ($-N_3$) have drawn a considerable attention mainly because of their role as primary agents in explosive reactions. If subjected to a sudden increase in temperature or a strong mechanical stimulus, they react violently, releasing a large amount of energy through the elimination of N_2 from the azide chain [1–3].

Furthermore, organic azides' applications cover a wide range of other areas [4], going from reactants in the preparation of superconducting materials [5] to biochemical applications as non-protonated inhibitors in human carbonic anhydrase [6,7]. More recently, the application of aryl-azides as photoaffinity labeling agents for proteins [8] or in phototherapy [9] of tumors and other lesions has enforced the general interest in these compounds.

The characterization of the electronic structure and the conformational analysis of the azides is thus of extreme importance to these subjects; the geometry of the molecules affects the nature of the valence orbitals, which in turn dictates the chemical properties of the compound. This is specially relevant if one wishes to study the activation of certain photochemical properties with changes in geometry [10] or the most stable conformers that favor a specific thermal decomposition pathway [11].

Although much has already been done in studying several azides systems, the aromatic ones, such as the benzyl azide (BA), lack the full theoretical and experimental characterization that already covered other simpler systems.

In this work, we analyze the character and energies of the outermost orbitals of benzyl azide (BA, $\Delta_f H^0_{gas} = 416$ kJ mol^{-1} [12]) and 2-, 3- and 4-methyl benzyl azide (2-, 3- and 4-MBA), based on theoretical results derived from quantum mechanical methods with different basis sets. The results will support the experimental work on these molecules, obtained with ultraviolet photoelectron spectroscopy (UVPES), namely by render possible the correct assignment of the bands. Additionally and in spite of the absence of experimental results on (1-azidoethyl)benzene (1-AEB) with UVPES, calculations on this molecule are also presented, in order to complete the theoretical study of the different isomers of the methylated benzyl azides.

As there are some known discrepancies between theoretical and experimental ionization values in aromatic systems [13], care should be taken on the direct, non-scaled, use of Koopmans' theorem; therefore, at least two *ab initio* methods and several basis sets combinations are used in order to assess the accuracy of the calculated results.

The structure of this paper is as follows: Section 2 details the nature and the methodology employed in the computations, Section 3 presents and discusses the results and Section 4 presents the most relevant concluding remarks.

2. Computational details

The Koopmans' theorem [14] was applied to the SCF orbital energies and the search for the optimum combination of method and basis was exclusively restrained to *ab initio* methods.

The Hartree–Fock (HF) and Møller–Plesset (MP2) methods [15–17] were employed with seven different basis sets – 6-31G(d,p), 6-31++G(d,p), 6-311++G(d,p), cc-pVXZ and aug-cc-pVXZ, where

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X = D,T . The first three are part of the commonly used Pople basis sets [18] which usually provide good results. The last four are referred as Dunning (correlation-consistent) basis set [19], and can include diffuse functions, emphasized by the prefix "aug". As shown further in this work, adding diffuse functions to the hydrogen atoms, and thus extending the spatial range of these atomic orbitals, changes the expected optimal geometry of the BA derivatives, specially if the N_3 chain is closer to the methyl group, like in 2-MBA.

The most complete and computational demanding basis set used in this work is the correlation-consistent, valence triple ζ, augmented by diffuse functions in the s, p and d atomic functions (aug-cc-pVTZ), constituted of 713 basis functions, which is expected to produce the best results, as it is the one that best approximates the complete-basis-set (CBS) limit.

Structure optimization of all parameters was accomplished through the standard optimization procedures in the Gaussian code, namely the Berny optimization procedure and the following threshold values for the maximum remaining force on an atom in the system, the average (RMS) force on all atoms, the maximum structural change of one coordinate (maximum displacement), and the average (RMS) change over all structural parameters in the last two iterations, respectively: 0.45×10^{-3}, 0.3×10^{-3}, 1.8×10^{-3}, 1.2×10^{-3}. The starting geometries to these optimizations correspond already to the lowest energy conformations and were taken from our previous studies [20].

All calculations were performed on our cluster, composed of one AMD Opteron 275 at 2.2 GHz as the master node and nine Intel Core2 Quad Q6600 at 2.4 GHz as computing nodes, running the Gaussian 03 [21] program in a Linux environment. The orbital pictures were created using the Molekel [22] program, and correspond to a isosurface value of 0.07.

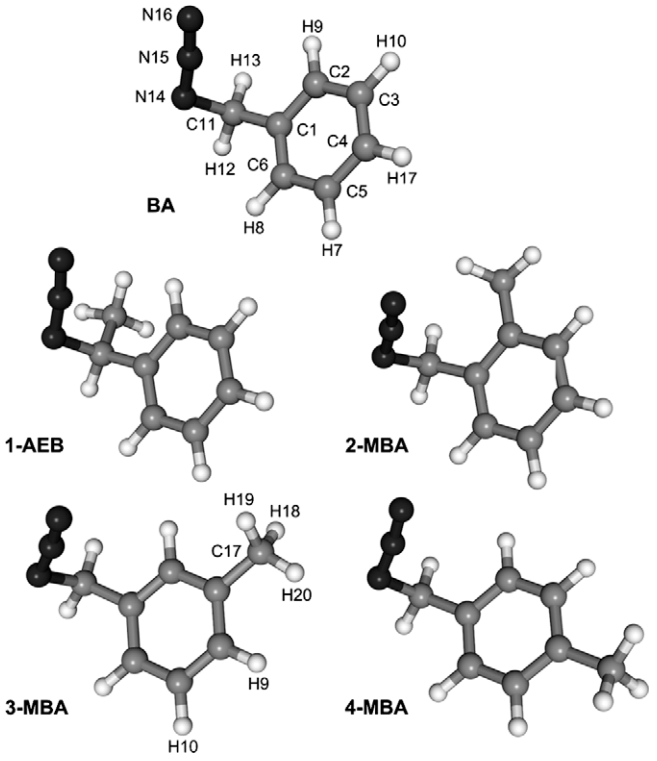

Fig. 1. Molecular structure of benzyl azide, (1-azidoethyl)benzene and 2-, 3- and 4-methyl benzyl azide. 3-MBA has the same labeling/numbering as BA, except for the atoms that are explicitly labeled differently in the figure. 1-AEB, 2- and 4-MBA share the same labeling/numbering as the 3-isomer.

3. Results and discussion

3.1. Molecular structure

The molecular structures of BA, its methyl derivatives and 1-AEB are depicted in Fig. 1. As stated earlier, the starting geometries for all optimizations were the ones obtained in a previous study; therefore only minor changes arose from the new optimizations with the different methods/basis set combinations.

The shown geometries correspond to the lowest energy conformers, where the benzene ring and the carbon atoms from the CH_2 and methyl groups reside in the same plane. The dihedral angle N_{15}–N_{14}–C_{11}– C_1 is always between 55° and 60°, except in the case of 2-MBA, in which its value goes down to approximately 35°, due to interactions between the nitrogen atoms and the methyl group. In 1-AEB, both azide and methyl groups step off the plane formed by the benzene ring, in opposite directions.

No symmetry group other than the trivial C_1 can be attributed to the molecules in study, at least in the lowest energy conformations; belonging to the C_S group could only occur with BA and 4-MBA, and only if the dihedral N_{15}–N_{14}–C_{11}– C_1 was 0° or 180° (and thus positioning the azide chain in a possible mirror plane that would cut the benzene ring through C_1, C_4 and C_{11}).

Table 1 presents a set of selected geometric parameters, obtained from the complete structure optimization of BA and its methyl derivatives, at the highest method/basis combination employed in this study – MP2/aug-cc-pVTZ.

3.2. Molecular orbitals and ionization energies

The molecular orbitals (MOs) of BA and its methylated compounds can be described in terms of the contributions of the MOs of benzene and azido groups [23,24]. Results arising from calculations with the MP2/6-311++G(d,p) method/basis combination provide a good qualitative description of the MOs shapes and orientations, whose contours are depicted in Fig. 2.

The first two MOs of the series (first and second columns of Fig. 2) originate mainly from the degenerate $1e_{1g}$ HOMO of benzene, which follows either a π_3 (HOMO of 4-MBA and BA's MO 34) or a π_2 (the remaining orbitals from the first and second columns) pattern.

The third and fourth MOs come from the azido group N_3: the third is comprised almost exclusively from the $\pi^*_{N_3}$ MO established in the nitrogen chain, whereas the fourth MO is a $\sigma^*_{N_3}$ that also features a very small σ_{CN} contribution. Considering the three outermost orbitals – $(11a')(12a')(3a'')$ – from the electronic configuration of methyl azide CH_3N_3, one can undoubtedly assign the third column MOs to the 3a″ state and the fourth column MOs to the 12a′ state.

The remaining MOs (fifth to seventh columns) correspond chiefly to several benzene orbitals, with more or less contributions from the nitrogens. MO 31 of BA and MO 34 of 2-, 3- and 4-MBA portrait a strong resemblance to the degenerate $3e_{2g}$ orbital (σ) of benzene. Also, MO 30 of BA and MOs 35 of 2-, 3- and 4-MBA are mainly constituted from benzene's $1a_{2u}$ orbital, following a π_1 pattern. The last column (MO 29 of BA and MO 33 in the case of the methyl derivatives) can also be attributed to another pattern of $3e_{2g}$. Finally, the character of 1-AEB orbitals follow the same scheme and ordering as in BA. These interpretations are summarized in the energy diagram of Fig. 3.

Table 2 accounts for the experimental ionization energies (IEs) of the first 5 bands of each compound. The theoretical IEs obtained from the optimized structures of Table 1 (computed with MP2/aug-cc-pVTZ) are also presented, for comparison. The experimental values of the IEs are taken from our recent UVPES study [25] on these molecules (except 1-AEB) and are reliable within an error margin of ±0.03 eV. Although this energy resolution could allow the study of