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Theoretical study of the molecular properties of benzyl azide, 2-, 3- and 4-methyl benzyl azide

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Abstract. Ab initio and density functional calculations have been performed to study the benzyl azide, 2-, 3- and 4-methyl benzyl azides. Several molecular properties, such as conformational equilibrium, optimal geometry, and vibrational frequencies, have been computed for these molecules. Ionisation energies were also computed.

PACS. 31.15.Ar Ab initio calculations – 33.15.Bh General molecular conformation and symmetry; stereochemistry – 33.15.Dj Interatomic distances and angles – 33.15.Ry Ionization potentials, electron affinities, molecular core binding energy

1 Introduction

The subject of compounds containing the azido group (-N_3) has been attracting great interest, both experimental [1–10] and theoretical [11–16]. Recent works have emphasised the potential use of azides in the preparation of superconducting materials [17], explosives [18] and biochemical applications as non-proponated inhibitors in human carbonic anhydrase [19]. On the other hand the dipolar character and relative instability of the azido group enables it to react in a variety of ways, depending on the molecular structure, reagents and experimental conditions [20,21].

The most recent theoretical studies have been based on ab initio and density functional methods [22–25].

It is well-known from experimental results that the first step in the thermolysis of azides involves nitrogen elimination to yield the respective imine as the co-product. The strong exothermic character of this step is responsible for the application of azides as important and useful synthetic reagents in many fields, especially in biology [26–28].

Currently there is considerable interest in the mechanisms of such decompositions [29]. The interest has arisen because of the potential use of these materials as high-energy storage sources in a number of industrial applications. Thus, the organic azides are important industrially in seismic explosives and useful propellants [30] and photoresistors [31]. On the other hand, because of their ability in the formation of highly reactive nitrene intermediates, they are also used as important reagents in semiconductor technology for insertion into otherwise stable chemical bonds — herein the thermal decomposition of organic azides is responsible for more uniform doping and improvement of the superconducting properties [32,33] and for the preparation of single-crystal gallium and silicon nitride epitaxial layers on semiconductors substrates at relatively low temperature [6].

The alkyne intermediates with benzyl azide via the dipolar cycloaddition provided the 1,2,3-triazyoles compounds [34–36]. This strain-promoted cycloaddition has been used to label biomolecules both in vitro and on cell surfaces without observable toxic effects, such as the the reaction of a derivatized cyclooctyne with benzyl azide [37]. Furthermore, as they are rigid azides, benzyl azides are also valuable nitrene sources. For example, low energy secondary electrons produce N_3^- by dissociative attachment to benzyl azide [38].

In spite of the large experimental efforts to understand the behaviour of such molecules, some fundamental questions regarding the mechanism of the thermal decomposition of such molecules are not completely answered.

Recent ab initio calculations [22,23] have illustrated that the conformational equilibrium and the prediction of ionisation energies of azides are extremely sensitive to the consideration of correlation effects. These calculations

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have also indicated which theoretical level seems appropriate for a discussion of the properties of azides and for comparison with experiment. However, these previous studies have been initially directed towards a series of simple azides. In this work we concentrate on more complex azides, namely the aromatic azides.

Very little is known about the properties of aromatic azides. To date only few theoretical ab initio calculations focusing on the prediction of the photo-chemistry of aromatic azide behaviour have been performed [39]. These calculations indicated that second–order Møller–Plesset perturbation level of theory provides an adequate theoretical framework to study simple organic azides. This conclusion is particularly important in the study of complex organic azides like aromatic ones, for which full ab initio optimizations at electronic correlated levels may demand a very large computational effort.

The present study reports ab initio and density functional calculations of the molecular properties of benzyl azide (BA) and its 2-, 3- and 4-methyl (2-, 3-, 4-MBA) isomers. We report on detailed analysis of several molecular properties of these molecular systems, such as conformational equilibrium structure and ionisation energies.

The main objective of the present study is to provide accurate theoretical results for molecular properties of these molecules, as part of a general study of thermal decomposition of presented aromatic azides by Ultraviolet Photoelectron Spectroscopy (UVPES) and Matrix-Isolation Infrared Spectroscopy.

Section 2 details the computational framework in which the calculations have been carried out. Section 3 presents and analyses the results for the molecular properties. The conclusions are presented in Section 4.

2 Computational details

To study the dependence on correlation effects, the molecular properties of the studied BA molecule have been computed in the framework of several quantum models, namely at the Hartree–Fock (HF) level, at the second–order Møller–Plesset perturbation level of theory (MP2) [40] and with the density functional theory (DFT), using the standard 6-31G** basis sets. Density functional calculations have been performed with the Lee, Yang and Parr correlation functional [41] together with either the Becke (BLYP) [42] or the Becke's three parameter (B3LYP) [43] exchange functionals.

In what concerns the 2-, 3-, 4-MBA molecules the calculations have been carried out at the HF and MP2 levels using the standard 6-31G** basis sets.

The energy of some structures were also computed at the coupled cluster level using single and double substitutions (CCSD) [44].

The HF, MP2, BLYP and B3LYP calculations were performed with the GAUSSIAN 98 program [45] on a IBM RISC/6000 and a PC/Pentium III 1 GHz workstations. The CCSD calculations were performed on a double CPU AMD Opteron Dual Core 2.2 GHz workstation.

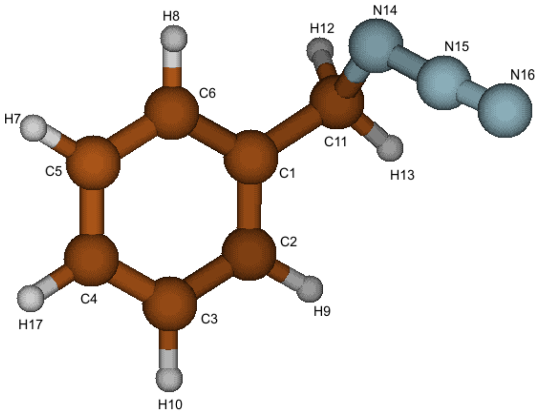

Fig. 1. Molecular structure of benzyl azide.

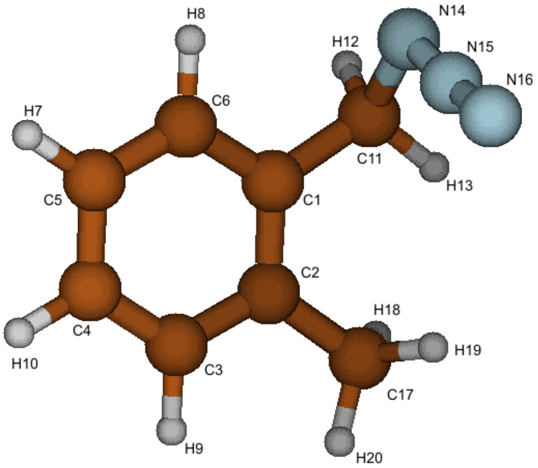

Fig. 2. Molecular structure of 2-methyl benzyl azide.

The optimization procedure and numerical thresholds used were the standard ones provided by 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: 0.000450, 0.000300, 0.001800, 0.001200.

3 Results and discussion

3.1 Structure

We performed the first conformational study of the BA, 2-MBA, 3-MBA and 4-MBA molecules in order to detect the minimum energy structure of each molecule. The structures of these four azides molecules are displayed in Figures 1, 2, 3, and 4, respectively.

Figure 5 shows the rotational potential $V(\phi)$ for the BA molecule obtained with several theoretical methods, by varying the N_{15}–N_{14}–C_{11}–C_1 dihedral angle (ϕ), using the same basis set (6-31G**). In this figure a quasi-symmetry of the curves around the conformer $\phi = 180^\circ$ is

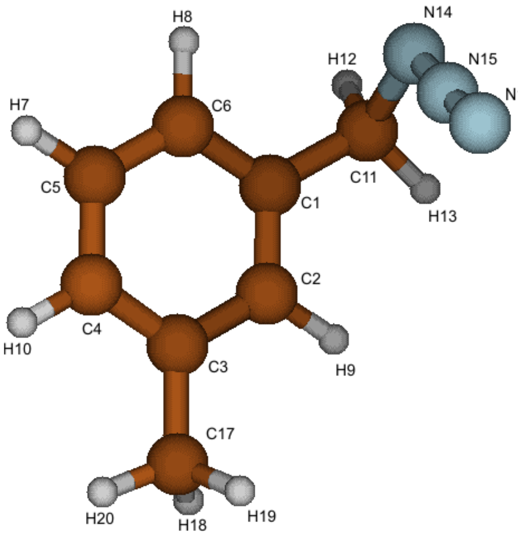

Fig. 3. Molecular structure of 3-methyl benzyl azide.

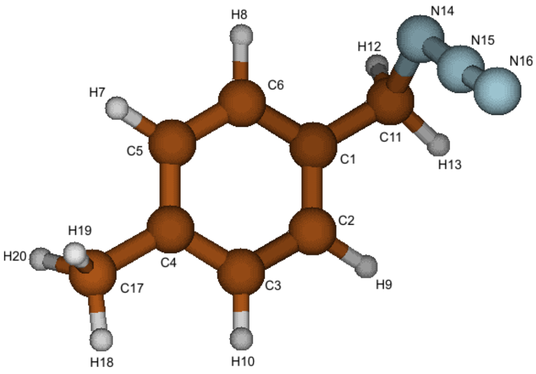

Fig. 4. Molecular structure of 4-methyl benzyl azide.

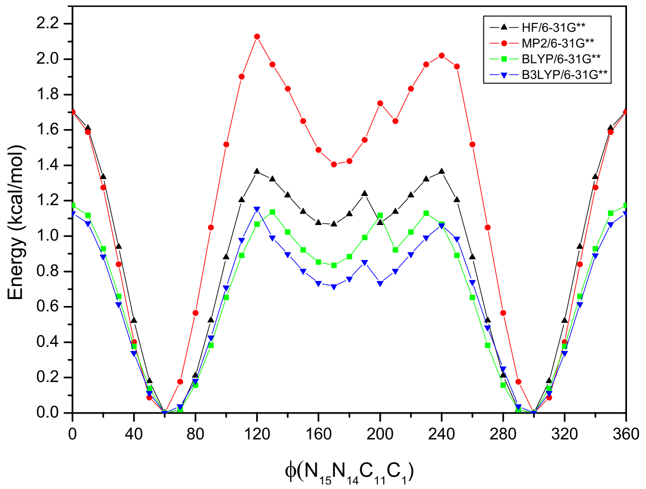

Fig. 5. Rotational potential of the benzyl azide as a function of the $N_{15}N_{14}C_{11}C_1$ dihedral angle.

Table 1. Optimized geometries of the benzyl azide obtained at several theory levels using the 6-31G** basis.

	HF	MP2	BLYP	B3LYP	CCSD
Bond length (Å)					
r^*_{1-2}	1.38	1.40	1.41	1.40	1.40
r_{1-11}	1.51	1.50	1.52	1.51	1.51
$r_{2-9^\S}$	1.08	1.08	1.09	1.07	1.09
r_{11-12}	1.08	1.09	1.10	1.09	1.09
r_{11-13}	1.09	1.09	1.10	1.10	1.10
r_{11-14}	1.48	1.49	1.51	1.49	1.49
r_{14-15}	1.23	1.25	1.25	1.24	1.25
r_{15-16}	1.10	1.16	1.16	1.14	1.14
Valence angles (deg)					
a_{1-2-9}	119.81	119.65	119.60	119.61	119.75
a_{1-6-8}	119.45	119.47	119.44	119.43	119.48
$a_{1-11-12}$	110.52	111.52	111.24	111.09	111.08
$a_{1-11-13}$	109.33	110.97	110.78	110.56	110.57
$a_{1-11-14}$	114.30	111.82	113.73	113.69	112.96
a_{2-1-11}	120.86	120.13	120.59	120.64	120.69
a_{6-1-11}	120.24	120.39	120.45	120.37	120.06
$a_{11-14-15}$	113.30	113.45	115.82	115.39	112.68
$a_{12-11-13}$	111.34	108.37	107.95	107.71	107.69
$a_{12-11-14}$	104.18	104.36	103.45	103.86	104.33
$a_{13-11-14}$	106.42	109.56	109.34	109.59	109.92
$a_{14-15-16}$	175.37	173.46	172.24	173.35	174.08

$^*r_{1-2}=r_{1-6}=r_{2-3}=r_{3-4}=r_{4-5}=r_{5-6}$

$^\S r_{2-9}=r_{3-10}=r_{4-17}=r_{5-7}=r_{6-8}$

evident, as expected from the geometry of the molecule. The only feature that prevents this symmetry to be total is the peak around $\phi = 200^o$.

By comparing the MP2 and HF results, it can be seen in Figure 5 that inclusion of electronic correlation increases the energy between the conformers. The largest difference is the barrier between the conformers $\phi = 120^o$ and $\phi = 240^o$, which are about 0.76 kcal/mol and 0.66 kcal/mol, respectively. In contrast, the DFT methods lead to energies of the conformers smaller than the HF ones.

The most stable structures of the BA molecule are predicted to be the conformers $\phi = 60^o$ and $\phi = 300^o$ by all methods. A full optimization of the (singlet) ground state of the conformer $\phi = 60^o$ has thus been carried out for this molecule.

Results for the optimized geometry of the BA molecule are listed in Table 1. Comparison between the results at HF/6-31G** and MP2/6-31G** levels show that electronic correlation contributes, in general, to an increase of some bond lengths of the order of 10^{-2} Å. Another modification related to the introduction of electronic correlation in the geometry optimization concerns the bending of the azide chain $a_{14-15-16}$ that is decreased at the MP2 level by ~2 degrees. Other significant modifications occur in the $a_{1-11-14}$, $a_{12-11-13}$ and $a_{13-11-14}$ angles that are changed by ~2.5, ~2.6 and ~–3.1 degrees, respectively, when we compare MP2 and HF results.

A comparison between the results at the HF/6-31G** level and the results at the remaining levels lead to almost the same conclusions; they differ only in the magnitude of the differences. The bigger discrepancy occurs in the $a_{1-11-14}$ angle, for which the differences are ~0.6, ~0.6 and ~1.3 degrees when compared to the BLYP, B3LYP and CCSD levels, respectively.

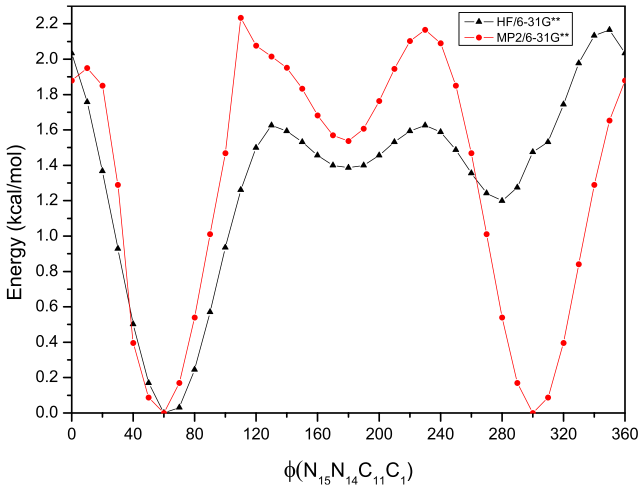

Fig. 6. Rotational potential of the 2-methyl benzyl azide as a function of the $N_{15}N_{14}C_{11}C_1$ dihedral angle.

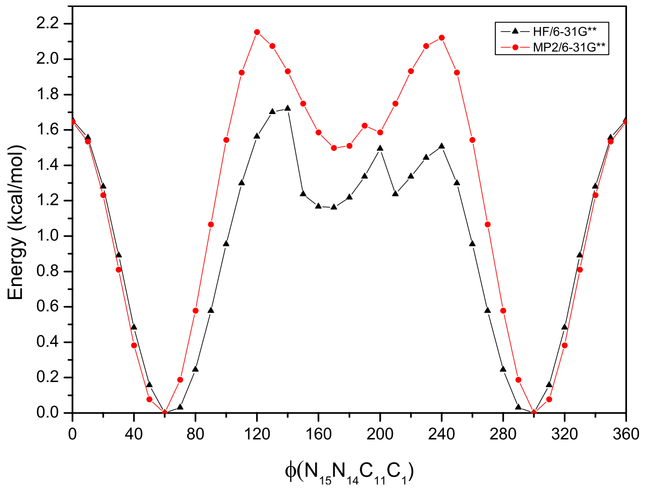

Fig. 8. Rotational potential of the 4-methyl benzyl azide as a function of the $N_{15}N_{14}C_{11}C_1$ dihedral angle.

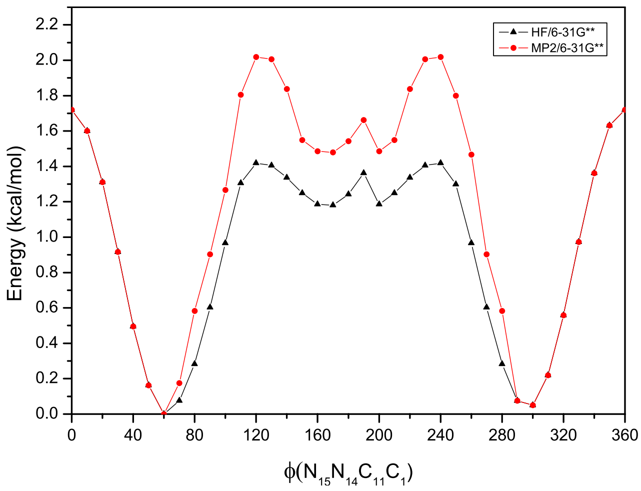

Fig. 7. Rotational potential of the 3-methyl benzyl azide as a function of the $N_{15}N_{14}C_{11}C_1$ dihedral angle.

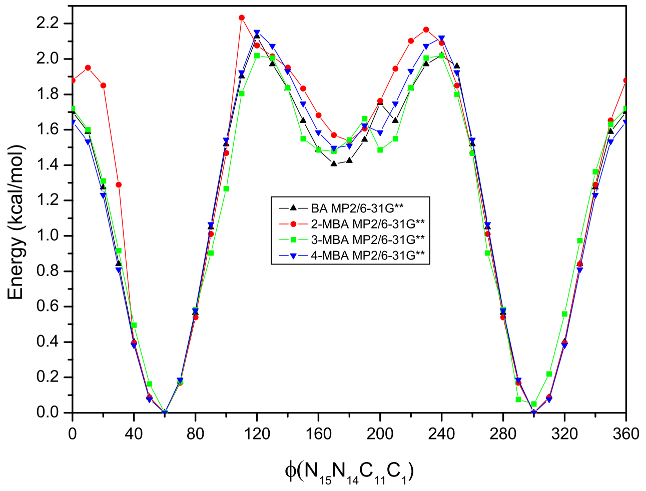

Fig. 9. Rotational potential of the benzyl azide and of the 2-, 3-, and 4-methyl benzyl azide as a function of the $N_{15}N_{14}C_{11}C_1$ dihedral angle.

Figures 6, 7 and 8 show the rotational potential $V(\phi)$ for the 2-, 3-, and 4-MBA, obtained with the HF and MP2 theoretical methods by varying the N_{15}–N_{14}–C_{11}–C_1 dihedral angle (ϕ), using the 6-31G** basis set.

These figures reveal in general the same trend that was observed in Figure 5 for the BA molecule. They exhibit a quasi-symmetry of the curves around the conformer $\phi = 180°$ and the corresponding most stable structures predicted by the two methods are found to be the conformers $\phi = 60°$ and $\phi = 300°$.

The most significant difference occurs in the 2-MBA molecule at the HF level, as seen in Figure 6. This may reveal the importance of the correlation in the 2-MBA molecule, in which the CH_3 group is close to the N_3 group.

In Figures 7 and 8 we observe a peak around $\phi = 200°$, which corresponds to the one mentioned in Figure 5 for the BA. This feature may be interpreted as a footprint of the azido group since it is evident in all azide molecules studied in this work, except for the 2-MBA molecule. The apparent omission of these peak in the later could be due to the closeness of N_3 group to the CH_3 group, which may mask the mentioned effect.

As in the BA molecule case, a full optimization of the (singlet) ground state of the conformer $\phi = 60°$ has been carried out for the three isomers and the resulting optimized geometries are listed in Table 2.

3.2 Total and ionisation energies

Tables 3 and 4 report total energies of the relaxed neutral and singly ionised structures, adiabatic differences (ΔE) between the energies of these structures, and dipole moments (μ) for the molecules analysed in this work.

To assess the energy results obtained with the HF, MP2, BLYP and B3LYP methods with a more reliable method, the energy of the most stable structure of the BA molecule was computed at the CCSD level. We noticed that the MP2 result differs by about 0.007% when

Table 2. Optimized geometries of the 2-methyl benzyl azide (2-MBA), 3-methyl benzyl azide (3-MBA) and 4-methyl benzyl azide (4-MBA) obtained at several theory levels using the 6-31G** basis.

	2-MBA		3-MBA			4-MBA	
	HF	MP2	HF	MP	CCSD	HF	MP
Bond length (Å)							
r^*_{1-2}	1.39	1.40	1.39	1.40	1.40	1.39	1.39
r_{1-11}	1.52	1.50	1.51	1.50	1.51	1.51	1.51
$r_{2-9^\S}$	1.08	1.08	1.08	1.08	1.08	1.08	1.08
r_{11-12}	1.08	1.09	1.08	1.09	1.09	1.08	1.08
r_{11-13}	1.08	1.09	1.09	1.09	1.09	1.09	1.09
r_{11-14}	1.48	1.49	1.47	1.49	1.49	1.48	1.48
r_{14-15}	1.23	1.25	1.23	1.25	1.25	1.23	1.23
r_{15-16}	1.10	1.16	1.10	1.16	1.14	1.10	1.10
$r_{17-X^\dagger}$	2.17	1.51	1.51	1.51	1.51	1.51	1.51
$r_{17-18^\#}$	1.09	1.09	1.07	1.09	1.09	1.09	1.09
Valence angles (deg)							
a_{1-6-8}	118.86	118.95	119.47	119.69	119.51	119.57	119.55
$a_{1-11-12}$	109.96	110.72	110.52	111.61	111.00	110.64	110.59
$a_{1-11-13}$	111.50	112.13	110.02	110.98	110.43	110.02	109.97
$a_{1-11-14}$	113.99	112.01	114.14	111.85	113.08	114.22	114.21
a_{2-1-11}	122.66	121.68	120.85	119.90	120.83	121.10	121.09
a_{6-1-11}	117.82	118.22	120.25	120.53	120.37	120.61	120.60
$a_{11-14-15}$	113.45	114.54	113.19	113.40	112.59	113.20	113.19
$a_{12-11-13}$	107.09	108.01	107.34	108.40	107.81	107.32	107.32
$a_{12-11-14}$	104.00	103.99	104.16	104.37	104.38	104.08	104.12
$a_{13-11-14}$	109.83	109.62	110.33	109.38	109.39	110.22	110.30
$a_{14-15-16}$	175.43	172.76	175.40	173.58	174.10	175.44	175.45

* $r_{1-2} = r_{1-6} = r_{2-3} = r_{3-4} = r_{4-5} = r_{5-6}$; § $r_{2-9} = r_{3-10} = r_{4-17} = r_{5-7} = r_{6-8}$;
† $X = 2, 3, 4$ for 2MBA, 3MBA and 4MBA, respectively; $^\#$ $r_{17-18} = r_{17-19} = r_{17-20}$.

Table 3. Molecular properties of the benzyl azide (BA) obtained at several theory levels.

	Total energy (Hartree)		ΔE (eV)	μ (D)
	BA	BA$^+$		
HF/6-31G**	−432.42	−432.13	7.70	2.03
MP2/6-31G**	−433.86	−433.52	9.42	2.36
BLYP/6-31G**	−435.01	−434.71	8.06	2.59
B3LYP/6-31G**	−435.16	−434.84	8.45	2.48
CCSD/6-31G**	−433.83	—	—	2.23

Table 4. Molecular properties of the 2-methyl benzyl azide (2-MBA), 3-methyl benzyl azide (3-MBA) and 4-methyl benzyl azide (4-MBA) obtained at several theory levels.

	Total energy (Hartree)		ΔE (eV)	μ (D)
	2-MBA	2-MBA$^+$		
HF/6-31G**	−471.46	−471.18	7.65	2.16
MP2/6-31G**	−473.05	−472.71	9.09	2.28
	3-MBA	3-MBA$^+$		
HF/6-31G**	−471.47	−471.19	7.60	2.26
MP2/6-31G**	−473.05	−472.72	8.88	2.44
CCSD/6-31G**	−473.09	—	—	2.49
	4-MBA	4-MBA$^+$		
HF/6-31G**	−471.47	−471.21	7.12	2.30
MP2/6-31G**	−473.05	−472.72	8.96	2.61

compared to the CCSD result. This agreement allows us to consider that the MP2 method is an accurate method for these molecules, being, by far, more manageable and less time consuming than the CCSD method. The same procedure was followed for one of the methyl benzyl azide isomers, the 3-MBA, with the CCSD method. In this case, the difference between the MP2 and the CCSD results is about −0.009%, which contributes for confirming the validity of the results calculated at the MP2 level.

We observe that ionisation energy values ΔE are dependent on the theoretical level of calculation. Dipole moments show some dependence on electronic correlation, in agreement with the results for the structure.

It should be emphasized that the ΔE values of the 2-MBA and 3-MBA molecules differ by less than 0.1 eV (1.3%) from the corresponding BA molecule at each theoretical level. On the other hand, the ΔE value of the 4-MBA molecule differs by about 0.6 eV (7.8%) from the corresponding value of the BA molecule. Thus, with such small energy differences a very precise experiment is needed in order to identify each of these molecules.

We notice that the ionisation energies based on Koopman's theorem are about 1 eV higher than the ΔE value computed in this work. For example, the ionisation energy value based on Koopman's theorem for the BA molecule at HF level was found to be ~9.08 eV, which is about 1.37 eV higher than the ΔE value computed in this work.

UVPES experiments, still in progress, will allow for the usual comparison between theoretical and experimental ionisation energies of the studied molecules.

4 Conclusions

We obtained in this work several molecular properties of the benzyl azide and its three methyl isomers, such as conformational equilibrium structure and ionisation energies. The most important conclusion is that the presence of the CH_3 group attached to the aromatic ring does not affect the relative conformational position of all four compounds.

Furthermore, since their adiabatic differences are very similar to each other, there is a need for an experiment with an energy resolution smaller than 0.1 eV in order to distinguish between these molecules.

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