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Molecule and Radical Structures of Isobutyronitrile

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Abstract

Molecule and radical structures of Isobutyronitrile were studied by DFT computations. Results of conformational analysis performed by combination of molecular mechanic and B3LYP/6-311++G(d,p) methods showed that isobutyronitrile inelastic molecule which has only one conformer. Using this structure, radical structure was investigated. Possible radicals were modelled and the experimental Electron Paramagnetic Resonance parameters were calculated. The calculated parameters obtained from B3LYP/TZVP computations were compared with the experimental counterparts which were taken from literature. Determined Molecule and Radical structures were given in this study.

1. INTRODUCTION

All physical and chemical properties of a molecule are related to molecular structure. Therefore, molecular structures are investigated firstly by X-ray diffraction, electron diffraction and microwave spectroscopy methods when a new molecule is synthesized. Furthermore, molecular structures can be determined by molecular modelling techniques[1-3]. Structure of many molecules, whose structures have not been determined or could not be determined before using experimental techniques, can be determined by molecular modelling techniques. Not only molecular structures of molecules, but also structures of all possible conformations can be identified by these techniques[1-3]. The effective molecular modeling technique for determining the molecular structure is to scan the potential energy surfaces. This technique is also known as conformational analysis in literature [1-3]. To the best of our literature survey, there is no published experimental data on the structure or the spectra of isobutyronitrile.

Radical is an atom, molecule or ion that has unpaired valence electrons. EPR spectroscopy is one of the most powerful methods in studying the structure and determining the identity of molecules containing unpaired electrons. There are two EPR parameters that contain valuable information about the geometry and electronic structure of the radical systems. One of them is known as isotropic hyperfine coupling constant (ihfcc), which is symbolized by A, another is isotropic g value. Extraction of these parameters from experimental spectra is not always straightforward. Beside, while radical types can be determined using these parameters, detailed radical structures cannot be determined [4-5].

Experimental EPR study of isobutyronitrile was performed [6], and four identical hydrogen splittings (20.72 G) and one nitrogen splitting (3.35G) were observed. G value was measured as 2.00290. After possible radicals are modelled, the structure of the radical having compatible parameters with these experimental values can be determined.

This study provides the first information on molecule and radical structures of these properties for isobutyronitrile. Determination of the modelled radical which has similar EPR parameters compatible with

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*Corresponding author, e-mail: odereli@konya.edu.tr experimental values will support the accuracy of the molecular structure identified for the first time in this study.

2. COMPUTATIONAL

This study was started with the conformational distribution calculation by choosing molecular mechanic method in Spartan 14 program [7]. The Obtained conformers were optimized by B3LYP method [8-10] and standart 6-311++G(d,p) basis sets in Gaussian 03 program[11] .After the most stable molecular structure was determined, possible radicals were modelled. Conformational analysis of model radicals were performed separately for each model radical using above procedure. Using the most stable forms of the model radicals, EPR parameters of them were calculated using B3LYP method and standart TZVP basis sets [12].

3. RESULTS AND DISCUSSION

To determine the correct radical structure, it is necessary to determine the correct molecular structure primarily. For this purpose, The calculations were started with the conformational analysis. At the beginning of conformation analysis, an input file was created in Spartan 14 program using the structural formula of molecule. Giving 10-degree rotations to each single bond of the structure in the input file, conformational distribution calculation was performed by molecular mechanical methods. As a result of calculations, four different conformations were obtained. To determine the structures and energies of these four conformers more precisely, which were obtained by relatively coarse method (Molecular mechanic), geometry optimizations of them were performed by Gaussian 03 program using B3LYP method and 6-311++G(d,p) basis set. The result geometry optimizations showed that the energies and structures, given in Figure 1, of these four conformers were the same.

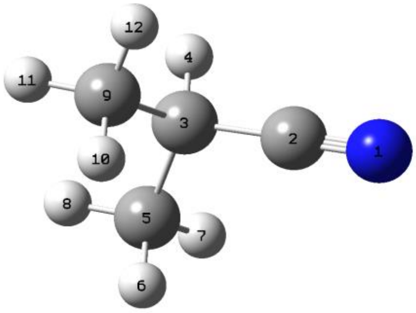


Figure 1. *Molecular Structure and Atom numbering scheme of isobutyronitrile*

Namely, all conformers were overlap by -211.4455295 Hartree energies and 4.1921 dipol moments . Therefore, it can be concluded that isobutyronitrile has only one conformer and it is not a flexible molecule. The calculated structural parameters of the title compound reported in Table 1 may serve as useful information in future electron diffraction or microwave studies of the compound.

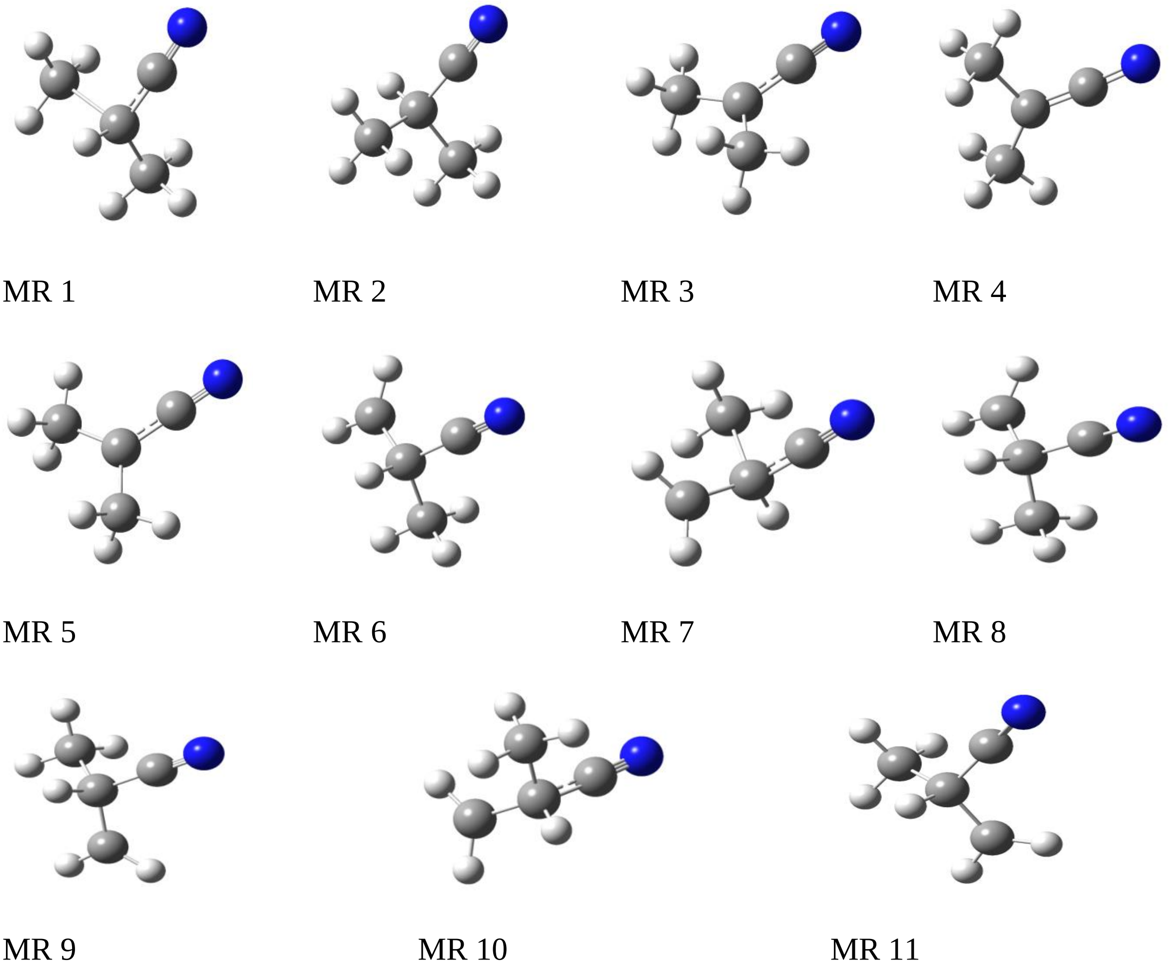
Table1. *Calculated Geometry parameters of Isobutyronitrile*

Bond lengths (A°)		***Bond angles (^{0})***		***Dihedral angles (^{0})***	
R(N1,C2)	1.154	**A(C5,C3,C9)**	112.3	**D(H4,C3,C5,H6)**	179.6
R(C2,C3)	1.468	**A(C3,C5,H6)**	110.7	**D(H4,C3,C5,H7)**	59.1
R(C3,H4)	1.096	**A(C3,C5,H7)**	111.3	**D(H4,C3,C5,H8)**	-60.9
R(C3,C5)	1.541	**A(C3,C5,H8)**	109.6	**D(C9,C3,C5,H6)**	-60.5
R(C3,C9)	1.541	**A(H6,C5,H7)**	108.3	**D(C9,C3,C5,H7)**	179.0
R(C5,H6)	1.093	**A(H6,C5,H8)**	108.4	**D(C9,C3,C5,H8)**	59.0
R(C5,H7)	1.092	**A(H7,C5,H8)**	108.5	**D(C2,C3,C9,H10)**	-63.5
R(C5,H8)	1.093	**A(C3,C9,H10)**	110.7	**D(C2,C3,C9,H11)**	177.0
R(C9,H10)	1.093	**A(C3,C9,H11)**	109.6	**D(C2,C3,C9,H12)**	57.1
R(C9,H11)	1.093	**A(C3,C9,H12)**	111.3	**D(H4,C3,C9,H10)**	-179.6

R(C9,H12)	1.092	**A(H10,C9,H11)**	108.4	**D(H4,C3,C9,H11)**	60.9
Bond angles (^{0})		**A(H10,C9,H12)**	108.3	**D(H4,C3,C9,H12)**	-59.1
A(C2,C3,H4)	106.3	**A(H11,C9,H12)**	108.5	**D(C5,C3,C9,H10)**	60.5
A(C2,C3,C5)	110.5	**Dihedral angles (0)**		**D(C5,C3,C9,H11)**	-59.0
A(C2,C3,C9)	110.5	**D(C2,C3,C5,H6)**	63.5	**D(C5,C3,C9,H12)**	-179.0
A(H4,C3,C5)	108.5	**D(C2,C3,C5,H7)**	-57.1		
A(H4,C3,C9)	108.5	**D(C2,C3,C5,H8)**	-177.0		

Using the conformer1 obtained in the above calculations, eleven different radicals were modeled. Model Radical 1 (MR1) and MR2 are cationic and anionic forms of the molecule. MR3 is a neutral radical formed by abstraction of H4 atom from the molecule, MR4 and MR5 are cationic and anionic forms of MR3. MR6 is a neutral radical formed by abstraction of one hydrogen atom from a methyl group (H11) ,MR7 and MR8 are cationic and anionic forms of MR6. MR9 is a neutral radical formed by abstraction of one hydrogen atom from another methyl group (H8) ,MR10 and MR11 are cationic and anionic forms of MR9.

Because the experiment was performed in liquid phase, assuming that the radicals can turn easily around single bonds, conformational analysis of each model radicals were performed individually and the most stable ones were determined. The obtained radical structures were given in Figure 2.



MR 1 MR 2 MR 3 MR 4

MR 5 MR 6 MR 7 MR 8

MR 9 MR 10 MR 11

Figure 2. *Model Radicals*

EPR parameters of model radicals were calculated by B3LYP method and TZVP basis sets. Calculation results were given in Table 2 in comparison with experimental data.

Table 2. *The calculated and the experimental EPR parameters of Isobutyronitrile*

a_{iso}	MR 1	MR 2	MR 3	MR 4	MR 5	MR 6	MR 7	MR 8	MR 9	MR 10	MR11	Experimental
N(14)	2.967	3.281	3.538	4.435	3.521	-0.070	1.807	1.734	-0.070	1.807	1.734	3.35
H(1)	14.115	-1.336	----	----	---	41.249	16.567	22.204	41.247	16.535	22.215	
H(1)	-2.312	1.269	0.711	17.122	12.945	-21.825	3.017	-7.372	-0.709	-1.319	1.573	
H(1)	-3.229	-1.918	28.569	-0.187	12.995	-20.959	-5.191	-10.170	-1.011	6.639	0.864	20.72
H(1)	11.153	1.856	28.568	17.114	1.335	----	----	----	2.330	-0.923	-1.524	20.72
H(1)	1.616	1.847	28.565	14.038	12.945	-0.709	6.632	-1.524	-21.825	2.961	-10.166	20.72
H(1)	44.422	-1.920	28.569	14.054	12.986	2.329	-1.302	0.866	-20.959	-5.192	-7.366	20.72
H(1)	6.874	1.277	0.711	3.881	1.336	-1.011	-0.930	1.576	----	----	----	
g_{iso}	2.00581	1.99037	2.00311	2.00802	2.00223	2.00267	2.01093	1.98725	2.00267	2.01091	1.98727	2.00290

It is difficult to measure g-values more accurately than by 10^{-3}. Thus, a deviation of 500ppm between theory and experiment usually falls within the experimental error, and even an agreement with theory within 1000 ppm (1ppt) is considered satisfactory [13]. As it can be seen in Table 2, only MR3 has four identical hydrogen splittings and the calculated g value of this radical was lies in the experimental g value in the range of 1000ppm. The calculated geometry parameters of MR3 were given in Table 3.

Table 3. *Optimized geometry parameters of the MR3*

Bond lengths (A°)		***Bond angles (^{0})***		***Dihedral angles (^{0})***	
R(N1,C2)	1.170	**A(H4,C3,H8)**	119.8	**D(C2,C3,H4,C5)**	0.0
R(C2,C3)	1.388	**A(C3,H4,C5)**	112.5	**D(C2,C3,H4,H6)**	121.3
R(C3,H4)	1.498	**A(C3,H4,H6)**	110.1	**D(C2,C3,H4,H7)**	121.3
R(C3,H8)	1.498	**A(C3,H4,H7)**	110.1	**D(H8,C3,H4,C5)**	180.0
R(H4,C5)	1.090	**A(C5,H4,H6)**	108.6	**D(H8,C3,H4,H6)**	58.7
R(H4,H6)	1.097	**A(C5,H4,H7)**	108.6	**D(H8,C3,H4,H7)**	-58.7
R(H4,H7)	1.097	**A(H6,H4,H7)**	106.6	**D(C2,C3,H8,C9)**	121.3
R(H8,C9)	1.097	**A(C3,H8,C9)**	110.1	**D(C2,C3,H8,H10)**	121.3
R(H8,H10)	1.097	**A(C3,H8,H10)**	110.1	**D(C2,C3,H8,H11)**	0.0
R(H8,H11)	1.090	**A(C3,H8,H11)**	112.5	**D(H4,C3,H8,C9)**	58.7
Bond angles (^{0})		**A(C9,H8,H10)**	106.6	**D(H4,C3,H8,H10)**	-58.7
A(C2,C3,H4)	120.1	**A(C9,H8,H11)**	108.6	**D(H4,C3,H8,H11)**	180.0
A(C2,C3,H8)	120.1	**A(H10,H8,H11)**	108.6		

4. CONCLUSION

Molecule and Radical structures of isobutyronitrile were given for the first time in this study. The fact that the true radical type which has compatible EPR values with experiment is obtained increases the reliability of the molecule and radical structures which were obtained in this study. These structures will be useful for future experimental researchers of isobutyronitrile.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors

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