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A study of magnetic structure of some annulenes based on nuclear magnetic resonance spectroscopy using density functional theory (DFT)

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ABSTRACT

35 molecules, mostly annulene structures including neutral and charged structures, were examined in the present study; and stable structure of ground-state was achieved through density functional calculations by Gaussian software after optimizing all the structures, then, NICS and NMR calculations were made on them. In calculations related to NICS, isotropic values which were one angstrom above center of gravity of all rings were considered as a proper criterion for confirming aromaticity. The more those values are negative, the more the aromaticity will be and from among the examined parameters in the present study, NICZzz is better than other criteria for confirming aromaticity.

Keywords: *Annulene, Aromaticity, NICS, NMR, DFT.*

1. INTRODUCTION

Annulene refers to monocyclic polyene that is totally conjugated; their overall formula is CnHn where n is an even number or CnHn+1 where n is an odd number. Naming regulations of IUPAC is that annulenes with 7 carbon atoms or more are named as [N]-annulene, in which N represents the number of the carbon atoms in the ring. However, smaller annulenes are sometimes named using the same notation. For example, benzene is sometimes called just annulene [1]. Kekulé introduced benzene's ring structure in 1865. He used the term aromatic for these kind of compounds. One year later, Erlenmeyer synthesized other chemical aromatics similar to benzene. The concept of fluctuation of single and double bonds of benzene in 19th century was replaced with resonance between standard structures [2]. Hückel [3-4], based on molecular orbital theory, stated when the number of the π electrons of conjugatedmonocyclic polyene equals 4n+2, in which n is a whole number, those polyenes will have levels filled with π electrons; and are also stable systems. If n=0, the system has 2π electron; and exhibits stability such as Cyclopropyl cation. If n=1, Cycloheptatrienyl cation, and cyclopentadienyl anion are stable. Systems containing 4n π electrons are low stable. Cyclobutadiene with 4π electrons is just a transient compound. Cyclooctatetraene with 8π electrons exhibits similar properties to olefins. Altogether, cyclic polymethylenes consisting of 4n+2π electrons are aromatic. Density functional theory is a useful tool for calculating stable state energy in real models. Accuracy of such calculations depends on development of approximations for modifying/correcting density function [5]. Aromaticity, anti-aromaticity or non-aromaticity of annulene compounds in chemical shifts of these compounds in radio range is very important and provides a different chemical environment for this hydrogen [6, 7, 8].

NMR (nuclear magnetic resonance) is often a laboratory instrument for determining aromaticity of compounds. One of the ways for recognizing aromaticity is using chemical shifts [6]. NMR is a method showing aromatic, anti-aromatic or non-aromatic characteristic of annulenes, even when a molecular conjugated cut by single bonds is classified. A group of annulene compounds are homoaromatic compounds which are resulted from hydrocarbon species with 4n+2 conjugated and cyclic π electrons from CH_2 units in molecular ring [9]. In a study, the (anti) aromaticity of dehydroannulenes of various ring size was examined by ring current effect in 1HNMR spectra, and the aromaticity of annulenes dehydro and dehydro as well as anti-aromaticity of annulenes dehydro and deydro were proved [10]. In another study, a new approach was sought in order to assess the aromaticity in molecules with different ring sizes by comparing electron density and NICS scan, and the influence of electron density on the magnetic magnitude of pseudo atoms (Bq), NICS, was studied in detail by scanning electron density vs. NICSzz (the out-of-plane component of NICS). This study shed new light on the role of electron density on the magnitude of NICS [11].

2. COMPUTATIONAL DETAILS

First, the structures under study were extracted from Organic Chemistry book [12]. Table 1 shows the neutral and charged structures under study, mostly annulene structures.

Then, the preliminary structure as per the found structural formula, in the cited references, was plotted by gaussview software to be introduced to guassian software; next, the input file was saved in gif format and the optimization process was performed by gussian 2009 software. The optimized structures were determined through B3LYP method with 6-31++g (d,p) basis set and nmr=giao keyword, and the required data were extracted from output and the section related to SCF GIAO Magnetic shielding tensor, the data related to the isotropics and required elements XX, YY, ZZ [13]. In order to extract the data for all the annulenes, the main ring was examined, because resonance or ring current occurs in the main ring.

Table 1. Neutral and charged structures in this study.

Entry	Compound name
1	[12]-Annulene
2	Benzene
3	Circulene
4	Corannulene
5	Coronene
6	Cyclobutadiene
7	Helicene
8	[8]-Annulene
9	[14]-Annulene
10	[10]-Annulene
11	Cyclopropene
12	Cyclopentadiene
13	Cycloheptatriene
14	[16]-Annulene
15	[18]-Annulene
16	Acenaphthylene
17	Azulene
18	Benzo(a)pyrene
19	7-Methylbenz[a]anthracene
20	Naphthalene
21	Anthracene
22	Porphyrins
23	Sulflower [octacirculene]
24	Tetrazene
25	Pyridine
26	Pyrimidine
27	Pyrrole
28	Furan
29	Thiophene
30	Purine
31	Indol
32	Cyclopentadiene anion
33	Cycloheptatrienyl anion
34	Cyclobutadiene anion
35	Cyclobutadiene cation

2.1. Review of the point magnetic property in center of gravity of the rings in molecules under study.

Magnetic properties in the center of gravity of the ring represents the electrons spin or ring current related to δ bonds and π bonds. It means that the more negative is the degree of isotropic of the center of gravity of the ring, the greater the covering will be, so the degree of isotropic in terms of ppm of the pseudo element (Bq) is the best criterion in the magnetic property in the point where the pseudo atom Bq is located, i.e. the more negative it is, the greater the covering or ring current will be, and the aromaticity will be higher. In the point of center of gravity of the rings, the more negative is the isotropic, the electron spin ease or stronger ring spin or greater ring current will be observed. For the compounds which have a positive value, non-spin is observed which is called anti-aromaticity in organic chemistry, and the more negative is this value, spin or resonance will be greater and it is more aromatic in organic chemistry, and the more this value is closer to zero in center of gravity of the rings (intermediate state), the spin is not complete and it is non-aromatic. However, negativity does not certainly mean aromaticity, because both π spin and δ spin is influencing; and if they reinforce each other the degree of isotropic will be highly negative, and if they weaken each other, they approach non-aromaticity, i.e. zero. If only the share of δ is effective, and has a high negative value, it cannot be called aromatic, i.e. it has the ease of δ bond spin. Now, the diagrams related to isotropic related to center of gravity of the ring is reviewed. Diagram 1 reviews the isotropic (1) or point isotropic in center of gravity of the ring in neutral structures according to their number.

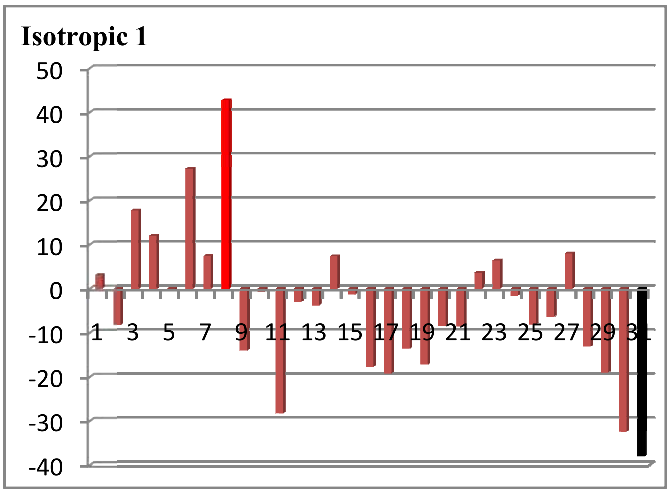

Diagram 1. Review of the isotropic 1 in neutral structures.

Diagram 1 reviews isotropic 1 in neutral structures. As it is shown in this diagram, its range varies in positive values from close to zero to 42.7 ppm and in negative values from below zero to -38.1 ppm, and it is inferred from this diagram that most structures have values close to zero and negative and less structures have positive values; and it can be concluded that the structures 1, 2, 3, 4, 6, 7, 8, 14, 22, 23 and 27 have positive values, and because there is non-spin of electron, they can be considered non-aromatic. The structures 2, 9, 11, 12, 13, 16, 17, 18, 19, 20, 21, 25, 26, 28, 29, 30 and 31 have negative values and it means they have ease of electron spin and there is higher resonance, so they are considered aromatic in organic chemistry. The structures 5, 10, 15 and 24 have values close to zero, and are considered non-aromatic according to this diagram.

Diagram 2 reviews the isotropic (1) or point isotropic in the center of gravity of the ring in charge structures according to their numbers.

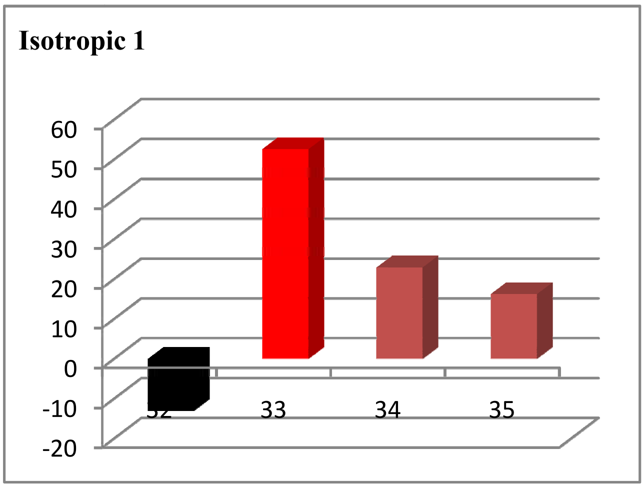

Diagram 2. Review of isotropic 1 in charged structures.

Diagram 2 reviews isotropic 1 in charged structures. As it is shown in this diagram, it has values in the range of -12.99 ppm at minimum and 52.6 ppm at maximum, and most of these structures have positive values. According to the definition of isotropic 1, structure 32 which has the minimum value can be considered aromatic and annulenes 33, 34 and 35 are not considered aromatic because of high positive values according to this diagram.

2.2. Magnetic properties in one angstrom above center of gravity of all the rings.

When we move away one angstrom from the center of gravity of the ring, no ring current due to sigma bond will be observed. The only cause of ring current in one angstrom above the ring is related to π orbitals or π bonds, i.e. the more the covering is or the more negative the isotropic (stronger field) is, the stronger the spin of the double bonds of π bonds will be, i.e. the aromaticity will be more determined by π bond. The isotropic difference in center of gravity of the rings and one angstrom above lies in the difference of the share of π orbitals and sigma orbital. In one angstrom above, the share of δ is minimum but in the center of gravity its share is maximum; for this reason, for the compounds which have a high δ spin, shows the central value of aromaticity, while they are not really aromatic because they do not have double bond. Thus, the best magnetic parameter for assessing aromaticity is the value of isotropic one angstrom above ring plane, and as we move further, the share of δ becomes weaker; the negative value of isotropic in this point only represents the spin of π bonds or electron located in it. Thus, the compounds having negative isotropic one angstrom above are described as aromatic by organic chemists or based on Hückel's rule [3-4]; but, given this criterion of isotropic 2 (its value), a comparison can be made between aromaticity properties of different aromatic compounds. For example, isotropic information for benzene shows that it is an aromatic compound but the aromaticity resulted from its π orbitals dominates the aromaticity resulted from δ orbitals. So its second isotropic is more negative than its first isotropic or in other words, in the center of the ring, electrons spin in δ bond slows down or weakens the movement of π electrons or reduces the covering in ring center of benzene. Therefore, isotropic value in ring center is -8.24ppm but in one angstrom above is -10.22 ppm. If δ spin did not weaken π, the value of first isotropic should have been more negative than the second isotropic; but we see it is not true about benzene. Whenever the molecule structure is planar, the best point for determining aromaticity of π bonds is exactly one angstrom above center of gravity of the ring, i.e. isotropic 2, but if the structure is non-planar, depending on the convexity and concavity of the non-planar structure, a point above the ring, that is a point different from isotropic one angstrom above the center of gravity will be selected such as isotropic 3 or 4 *etc*.

2.3. Comparing isotropic 1 and 2.

Whenever both isotropic 1 and isotropic 2 have negative values, the compound is certainly aromatic. But isotropic number 2 is much more negative than isotropic one, it means that double bond or π bond has a great resonance which is ideal aromaticity in organic chemistry, such as in benzene in which the value of isotropic 2 is more negative than the first isotropic.

2.4. Comparing isotropic 2 and 3.

Whenever isotropic 2 is more negative than isotropic 3, the compound is aromatic and planar. If isotropic 3 is more negative than isotropic 2, the compound is aromatic and non-planar (this is true for all monocyclic compounds or polycyclic fused structures such as anthracene). Now we review the related diagrams.

Diagram 3 reviews isotropic 2 and 3 in neutral structures according to their number.

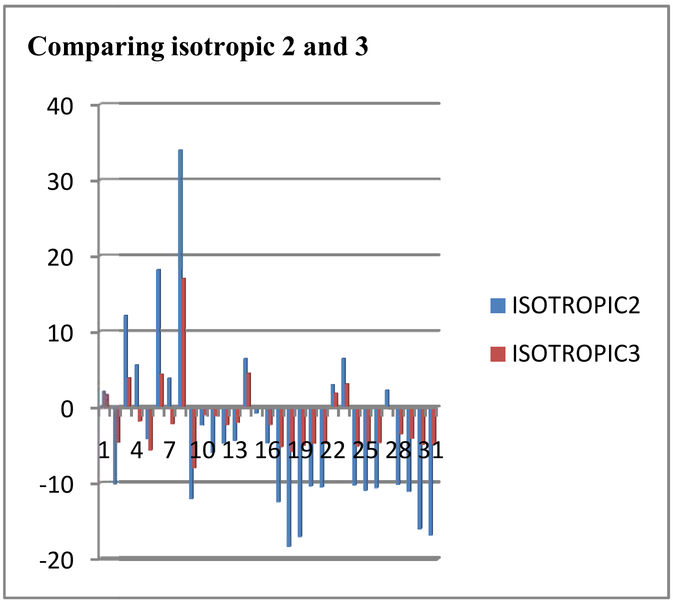

Diagram 3. Comparing isotropic 2 and 3 in neutral structures.

Diagram 3 reviews isotropic 2 and 3 in neutral structures and according to the diagram it includes both positive values and negative values. The isotropic 2 and 3 related to structures 2, 5, 9, 10, 11, 12, 13, 15, 16, 19, 20, 21, 24, 26, 28, 29, 30, 31 has negative values and since the values of isotropic 2 and 3 can help us in determining if the compounds are planar, the structures which have more negative isotropic, i.e. they are aromatic and planar, include structures 2, 9, 10, 11, 12, 13, 15, 16, 17, 18, 19, 20, 21, 24, 25, 26, 28, 29, 30 and 31 m and the structures which is aromatic and non-planar is structure 15, and other structures including 1, 3, 4, 6, 7, 8, 14, 22, 23 and 27 do not have the requirements according to Diagram 3. Diagram 4 reviews the isotropic 2 and 3 in charged structures according to their number.

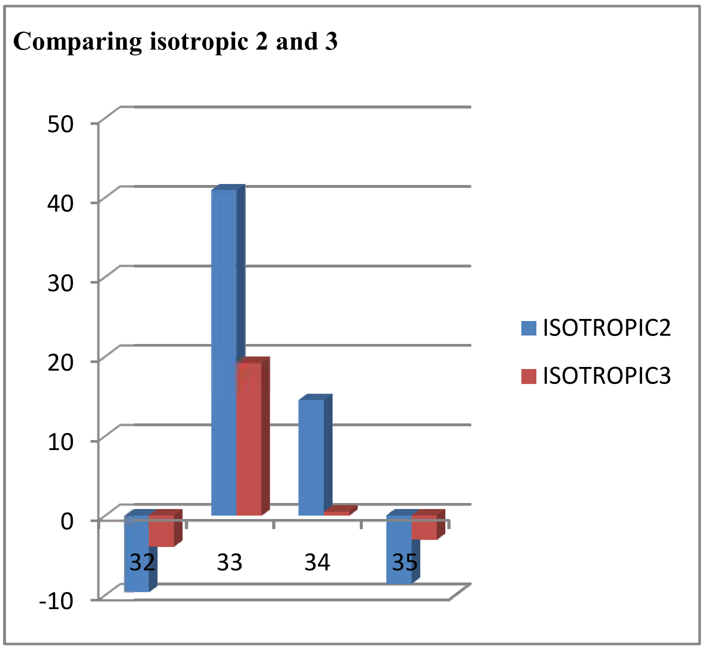

Diagram 4. Comparing isotropic 2 and 3 in charged structures.

Diagram 4 reviews the isotropic 2 and 3 in charged annulenes. As a result, annulenes 32 and 35 have the requirements of being aromatic and planar because their isotropic 2 and 3 is negative and in some way, the value of isotropic 2 is more negative than isotropic 3, but annulenes 33 and 34 do not have the requirements according to the diagram, so they are not aromatic.

A component of the isotropic (xx, yy, zz) which is toward the outer plane of the molecule, has the most effect on electron spin or their ability to move away from the molecule plane, i.e. the concept of aromaticity is more clarified by this out-of-plane component which is called NICS (ZZ) [14, 15, 16].

Table 2. NICS (ZZ) results.

Numbers NICS(ZZ)	Name Compound
-28.93	Benzene
-7.71	Coronene
-32.69	Annulene
-10.28	[10]-Annulene
-14.77	Cyclopropene
-12.1	Cyclopentadiene
-8.44	Cycloheptatriene
-3.58	[18]-Annulene
-17.41	Acenaphthylene
-30.05	Azulene
-39.3	Benzo(a)pyrene
-37.65	7-Methylbenz[a]anthracene
-28.79	Naphthalene
-28.66	Anthracene
-26.47	Tetrazene
-28.79	Pyridine
-27.32	Pyrimidine
-26.65	Furan
-28.86	Thiophene
-35.81	Purine
-39.18	Indol
-33.35	Cyclopentadiene anion
-10.61	Cyclobutadiene cation

Table 2 shows the aromatic compounds which exhibit aromaticity property based on isotropic 2, and indicates their NICS(ZZ) value (in fact, NICS (ZZ) is determined according to a component of isotropics XX2 or YY2 or ZZ2 which shows the direction out of the molecule's plane). In this table, the highest value of NICS (ZZ) is related to structure number 15 or [18]-Annulene and the lowest value or most negative value is related to structure 31 or Indol, which in fact, because of having more negative NICS (ZZ), can have the aromatic requirement more than other structures according to this table.

3. RESULTS SECTION

Now we review the diagrams 5 and 6 related to the review of isotropic one angstrom above center of gravity of the ring in neural and charged structures, and conclude as follows. Diagram 5 reviews isotropic one angstrom above center of gravity of the ring in neutral structures according to their number.

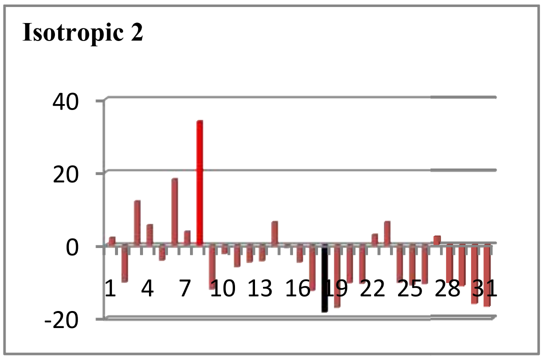

Diagram 5. Review of isotropic 2 in neutral structures.

Diagram 6 reviews isotropic one angstrom above center of gravity of the ring (isotropic 2) in charged structures according to their numbers.

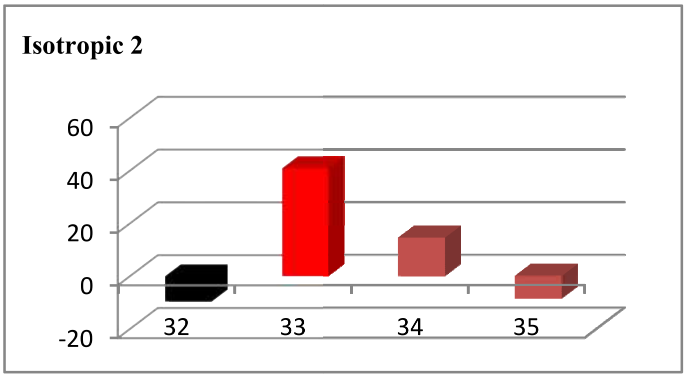

Diagram 6. Review of isotropic 2 in charged structures.

Most of the structures which are aromatic demonstrate negative values according to diagrams 5 and 6, which in fact, confirms their aromaticity. So it is concluded that the isotropic one angstrom above the center of gravity of the rings in the structures under study can be a relatively acceptable criterion for determining and confirming aromaticity and its properties.

Diagram 7 reviews isotropic 1 and 2 in neutral structures according to their number.

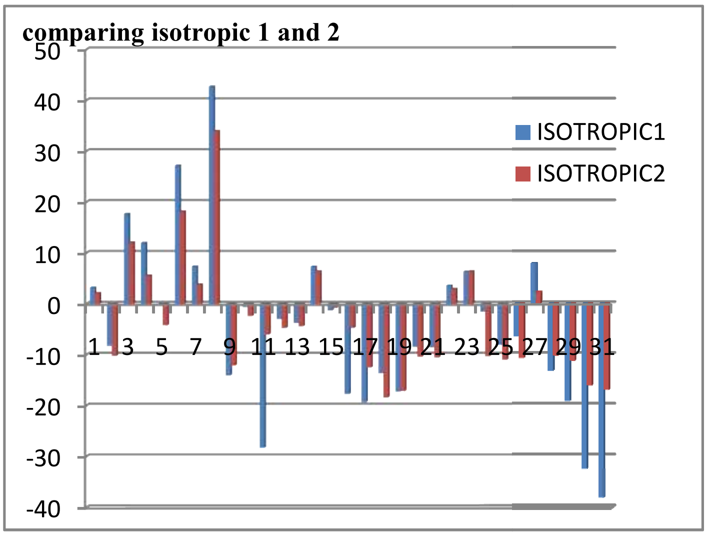

Diagram 7. Comparing isotropic 1 and 2 in neutral structures.

Diagram 8 reviews isotropic 1 and 2 in charged structures.

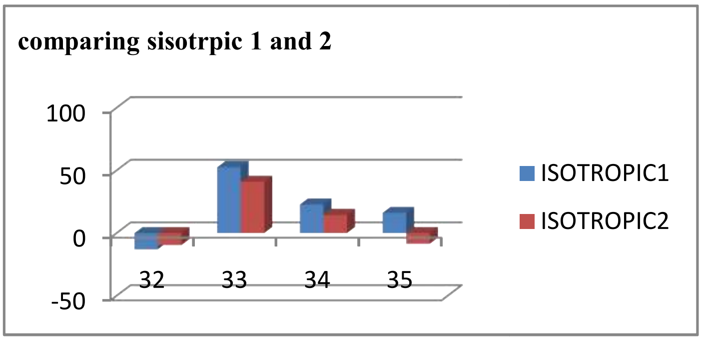

Diagram 8. Review of isotropic 1 and 2 in charged structures.

Given the review of neutral and charged structures in diagrams 7 and 8, it can be concluded that the criterion in these diagrams is the structures that their isotropic 2 is much more negative than their isotropic, i.e. in terms of organic chemistry, they are ideal aromatic. Therefore, from among all neural and charged structures available, the structures having this requirement are 2, 5, 12, 13, 18, 20, 21, 24, 25 and 26 and from among these the structure 24 has the most difference between negative isotropic 1 and 2, so it can be an idea aromatic compound.

Diagram 9 shows the NICS (ZZ) in neutral and charged structures under study.

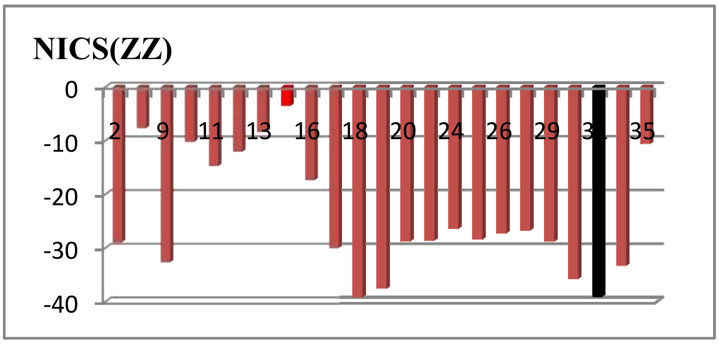

Diagram 9. Review of NICS (ZZ) in neutral and charged structures under study.

Given the data presented in diagram 9, it can be concluded that since NICS (ZZ) is more precise than isotropic 2, because there is no share of δ bond in it and π electrons spin area is outside the molecule's plane (it is because there is no internal resonances outside the ring), it can be a proper criterion for determining aromaticity in organic chemistry. The results shows that the diagram has a negative trend i.e. the aromaticity of these structures is confirmed by NICS (ZZ) and the most negative value is related to structure 31 and the minimum value is related to structure 51, so the most aromatic structure is structure 31 according to this diagram.

4. CONCLUSIONS

Based on the overall conclusion in this study it can be inferred that given the structures the negative value by isotropic 2 (a proper parameter compared to other examined isotropics in the present study for determining aromaticity), i.e. indicated the aromaticity property were also assessed by the NICS (ZZ). It can be actually be stated that NICS (ZZ) acts as a screen, i.e. every structure confirmed by the isotropic 2 and has the appropriate condition in terms of isotropic 2 elements are confirmed by NICS (ZZ); actually, NICS (ZZ) is determined based on an element of isotropics of XX2 or YY2 or ZZ2 directed toward the molecule plane and aromaticity is stated with more confidence. Therefore, NICS (ZZ) is better and more precise than isotropic 2, because there is no share of δ bond in it and π electrons spin area is outside the molecule's plane (it is because there is no internal resonances outside the ring). Thus NICS (ZZ) is a proper and better criterion for determining aromaticity, compared to other parameters examined in this study.

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