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Evaluation of the Aromaticity of a Non-Planar Carbon Nano-Structure by Nucleus-Independent Chemical Shift Criterion: Aromaticity of the Nitrogen-Doped Corannulene

A. Reisi-Vanani[*], **L. Alihoseini**

Department of Physical Chemistry, Faculty of Chemistry, University of Kashan, Kashan, Iran.

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**Corresponding author:*
E-mail address*:*
areisi@kashanu.ac.ir
Phone: +98 3155912358
Fax: +98 3155912397

Abstract

Substitution of two or four carbon atoms by nitrogen in the corannulene molecule as a carbon nanostructure was done and the obtained structures were optimized at MP2/6-31G(d) level of theory. Calculations of the nucleus-independent chemical shift (NICS) were performed to analyze the aromaticity of the corannulene rings and its derivatives upon doping with N at B3LYP/6-31G(d) level of theory. Results showed NICS values in six-membered and five-membered rings of two and four N atoms doped corannulene are different and very dependent to number and position of the N atoms. The values of the mean NICS of all N-doped structures are more positive than intact corannulene that show insertion of N atom to the structures causes to decreasing aromaticity of them.

1. Introduction

In recent years, understanding of the origin of aromaticity has been enormously interested [1]. Aromaticity has not precise quantitative definition and is not directly measurable experimentally. In other words, aromaticity is a virtual quantity, rather than a physical observable [2, 3]. Aromaticity is a manifestation of electron delocalization in closed circuits, either in two or in three dimensions that causes to energy lowering and a variety of other unusual chemical and physical properties. Since aromaticity is related to induced ring currents, magnetic properties are particularly important for its detection and evaluation. The imprecise nature of the aromaticity concept has stimulated the search for a quantitative definition and the development of numerous aromaticity criteria and indices [4, 5]. Since aromaticity is not a directly measurable quantity, its magnitude is now generally evaluated in terms of structural, energetic, and magnetic criteria. However, magnetic properties are the most closely related to aromaticity, they depend directly on the induced ring currents associated with cyclic electron delocalization [6, 7]. The most appropriate index of the aromaticity that has been seen in the literature is the magnetic criterion which is defined in terms of the ring currents induced when an aromatic/antiaromatic compound is placed in an external magnetic field [8, 9].

NICS is defined as the negative value of the absolute shielding computed at the ring center of a molecule (NICS(0)) or at some other point, usually at 1 A (NICS(1)) [10]. Negative NICS values in the center of the ring exhibit the presence of induced diatropic ring currents (aromaticity), whereas positive NICS values at the same points show paratropic ring currents (antiaromaticity) and NICS values close to zero belong to nonaromatic species.

Corannulene is a polycyclic aromatic hydrocarbon composed of five perifused aromatic ring around a central five-membered ring. Corannulene is one of the simplest curved carbon structures and can be represented as one third of a C60 fullerene molecule with hydrogen termination. Corannulene was first synthesized by Lawton and Barth in 1966 [11]. However, C20H10 remained silent until the discovery of Buckminsterfullerene by Kroto et al. in 1985

To our knowledge, aromaticity of the individual rings in corannulene N-doped derivatives that we have considered them in this study has not previously been investigated. Rogachev et al. through calculations of NICS values showed that the alkyl attachment at the hub-position does not change the aromaticity of six-membered rings (except increasing the aromaticity of one) but replaces the interior anti-aromatic five-membered ring in the neutral corannulene with the slightly aromatic one of a partially negatively charged cyclopentadienyl ring. But, the aromatic systems in spoke- and rim- isomers are mostly eliminated upon the electrophilic attack at these positions [12]. Frash et al. showed that protonation of corannulene at a hub carbon, according to the NICS analysis, makes the central ring aromatic, and enhances aromaticity of the peripheral rings. But, protonation at a rim carbon or a bridgehead rim carbon enhances antiaromaticity of the central ring, and reduces the average aromaticity of the peripheral rings [13]. Denis calculated the values of the NICS(0) for corannulene and two nitrogen disubstituted corannulene isomers and concluded that aromatic character of them is strongly dependent on the position of the nitrogen atoms. The results indicated that the aromaticity of an isomer diminished from that observed in corannulene and it has small aromatic character in the central pentagon and two hexagons; the antiaromatic character was seen for the remaining 3 hexagons. The later results are in contrast with the observed for corannulene, which has aromatic character in the hexagons and antiaromatic on the pentagon [14]. In this work, we used NICS criterion to describe the aromaticity of corannulene and its N-doped derivatives. We investigated the effect of N-doping on the aromaticity of the corannulene molecule.

2. Computational methods

In this study, the first considered model was the intact corannulene molecule and the other models resulted from the substitution of two (22 structures) and four (7 structures) carbon atoms by nitrogen atoms in the corannulene molecule. The geometry optimizations were performed using the second-order Moller–Plesset perturbation theory (MP2) with the 6-31G(d) basis set and vibrational frequency calculations were carried out at the same level of theory. No imaginary frequency was seen that confirmed them as a true minimum on the potential energy surface. The computational calculations were performed using the Gaussian 03 package [15] and the results were displayed using GaussView 5 software [16]. The gauge-independent atomic orbital (GIAO) NMR [17] calculations were calculated at B3LYP/6-31G(d) level of theory and then NICS values (in ppm) were computed from the magnetic shielding tensor that was calculated for ghost atoms located at the geometrical center of the rings to evaluate aromaticity, antiaromaticity and nonaromaticity. Negative, positive and nearly zero values of the NICS denote aromaticity, antiaromaticity and nonaromaticity, respectively [5, 18]

3. Results and Discussion

We calculated the NICS(0) values in all rings center of corannulene and its N-doped derivatives at the GIAO-B3LYP/6-31G(d) level of theory. In this study, we have focused on the NICS values for different rings of the two and four N atoms doped corannulene ($C_{18}N_2H_{10}$ and $C_{16}N_4H_{10}$) compared with intact $C_{20}H_{10}$. The aromaticity of the corannulene was previously studied to reveal that the six-membered rings are aromatic while the interior five-membered ring is antiaromatic [12-14]. Our NICS calculations for the intact corannulene yielded values +9.51 ppm for the five membered ring and almost –7.20 ppm for the six-membered rings that are in good agreement with literature. The computed NICS values in the center of rings of corannulene molecule have been shown in Fig. 1. Antiaromaticity character of the five-membered ring and aromaticity character of the six-membered rings were concluded from these values. The NICS values of the six-membered and five-membered rings are negative and positive that indicates their aromatic and antiaromatic character, respectively. Aromatic character of the intact corannulene will be concluded from mean value of the NICS that is equal to –4.48.

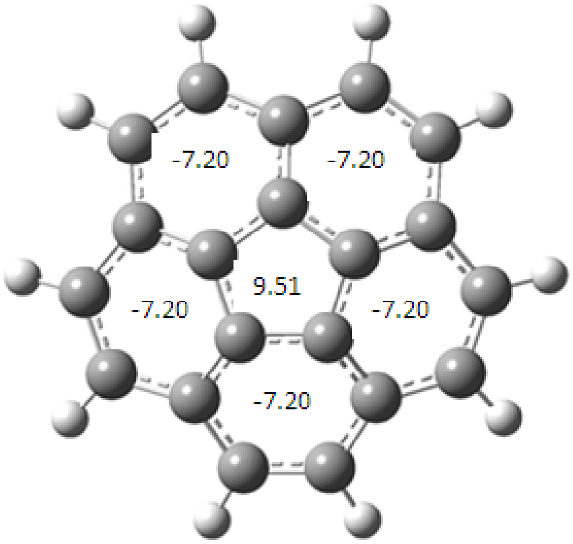
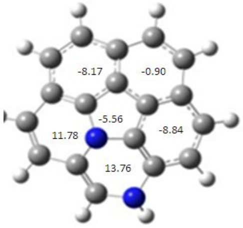


Fig. 1. NICS(0) values in the all rings of intact corannulene at the GIAO-B3LYP/6-31G(d) level of theory.

For evaluation of the effect of N-doping on aromaticity and antiaromaticity character of the corannulene derivatives, we substituted two or four C atoms in corannulene with N atoms. Determined NICS at rings center, NICS(0), for 2 N atoms doped corannulene (Structures **1-22**) and for 4 N atoms doped corannulene (Structures **23-29**) have been shown in Figs. 2 and 3, respectively. As shown in Figs. 2 and 3, NICS values in six-membered and five-membered rings of two and four N atoms doped corannulene are different and very dependent to number and position of the N atoms .

Average NICS values and relative energies of corannulene and its 2 and 4 N atoms doped



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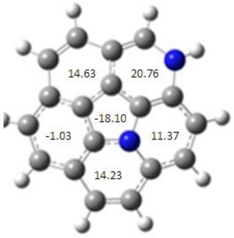

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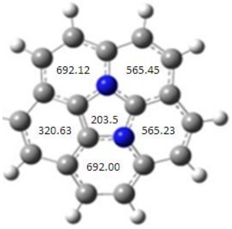

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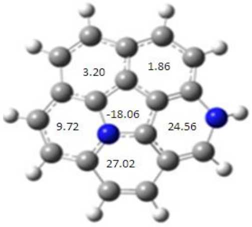

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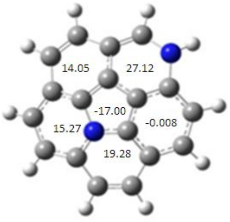

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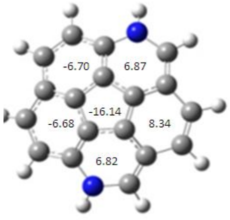

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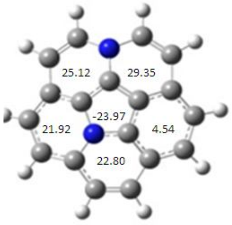

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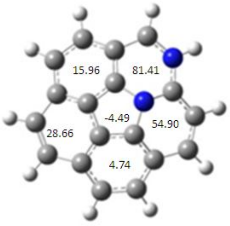

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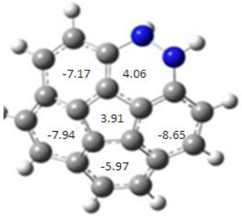

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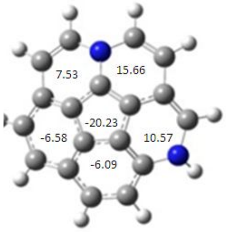

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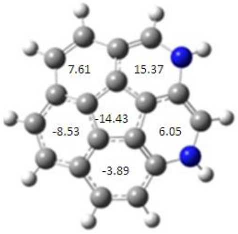

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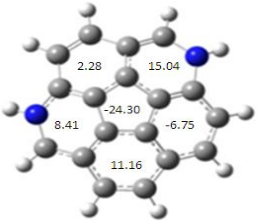

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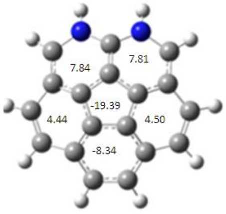

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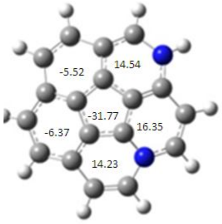

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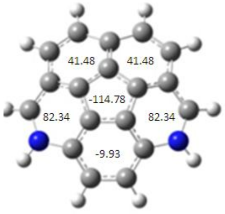

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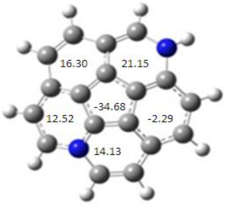

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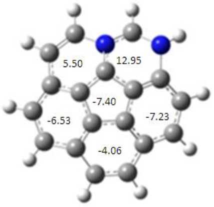

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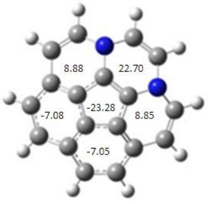

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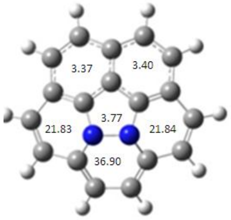

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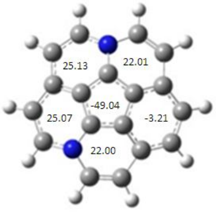

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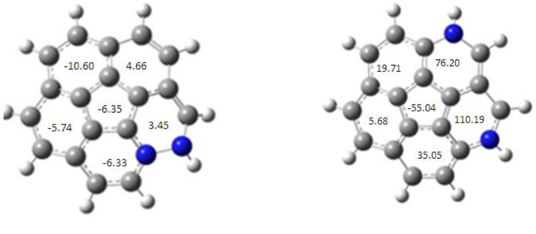
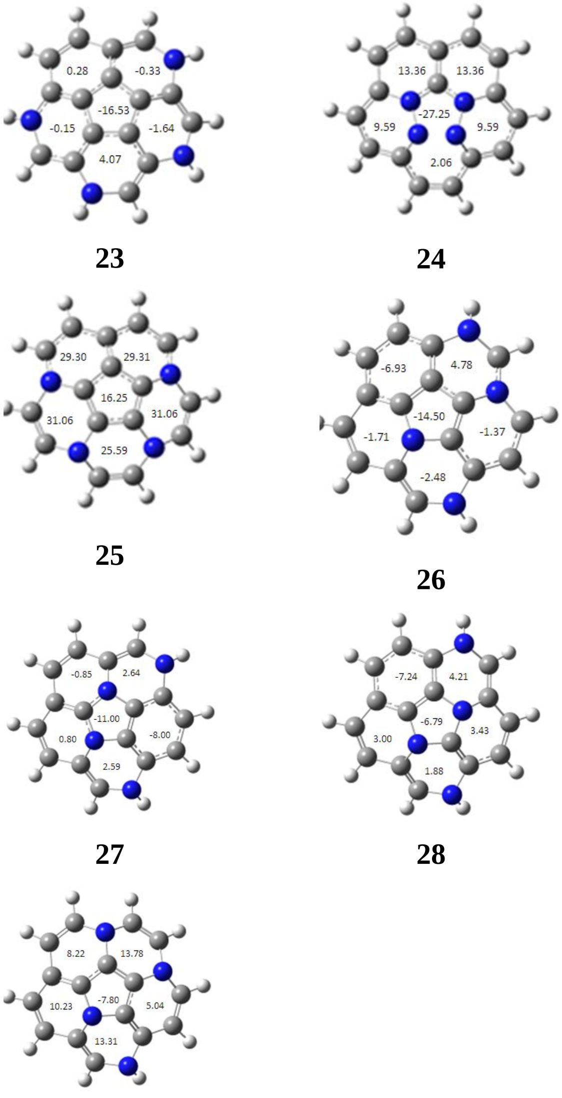


21 **22**

Fig. 2. NICS values in the all rings of structures **1-22** at the GIAO-B3LYP/6-31G(d) level of theory.

derivatives was been collected in Tables 1 and 2, respectively. Several structures (**3, 6, 13-15, 18-20, 24, 25** and **27**) have a plane of symmetry and their NICS(0) values on both sides of this plane must be almost identical. The values of NICS of all N-doped structures are more positive than intact corannulene that show insertion of N atom to the structures causes to decreasing aromaticity of them. Results show for two N atom doped corannulene, structures **9** and **21** with two adjacent N atoms are more aromatic structures, also existence of two N atoms in hub position cause to antiaromatic character so structure **3** is very antiaromatic. Though structure **19** has two adjacent N atoms and must be aromatic, but existence of two N atoms in hub position cause to be antiaromatic.



23 **24**

25 **26**

27 **28**

29

Fig 3. NICS values in the all rings of structures **23-29** at the GIAO-B3LYP/6-31G(d) level of theory.

Table 1. Relative energies (kcal/mol) and Mean NICS (ppm) of the $C_{18}N_2H_{10}$ investigated isomers.

Isomer	Relative energy (kcal/mol)	Mean NICS (ppm)
$C_{20}H_{10}$	-	-4.48
1	0.00	0.34
2	8.43	6.98
3	28.46	506.45
4	8.02	8.05
5	10.55	9.78
6	12.50	-1.25
7	15.49	13.29
8	22.99	30.20
9	16.96	-3.63
10	18.47	0.14
11	19.01	0.36
12	19.75	0.97
13	22.32	-0.52
14	25.27	0.24
15	36.38	20.49
16	28.08	4.52
17	28.32	-1.13
18	31.43	0.50
19	38.64	18.18
20	33.94	6.99
21	45.53	-3.49
22	31.67	31.96

Table 2. Relative energies (kcal/mol) and Mean NICS (ppm) of the $C_{16}N_4H_{10}$ investigated isomers.

Isomer	Relative energy (kcal/mol)	Mean NICS (ppm)
23	19.41	-2.38
24	83.29	3.45
25	25.11	27.1
26	22.37	-3.70
27	0.00	-2.57
28	6.88	-0.25
29	38.88	7.13

4. Conclusion

Calculated NICS values at rings center of 2 and 4 N atoms doped corannulene in six-membered and five-membered rings of them are different and very dependent to number and position of the N atoms. The values of NICS of all N-doped structures are more positive than intact corannulene that show insertion of N atom to the structures causes to decreasing aromaticity of them. Results show that structures with two adjacent N atoms doped corannulene are more aromatic structures, but existence of two N atoms in hub position cause to increasing of the antiaromatic character.

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References

[1] M. Elango, R. Parthasarathi, G. Karthik Narayanan, A.M. Sabeelullah, U. Sarkar, N. Venkatasubramaniyan, V. Subramanian, P. Chattaraj, J. Chem. Sci.117 (2005) 61-65.

[2] A.R. Katritzky, M. Karelson, S. Sild, T.M. Krygowski, K. Jug, J. Org. Chem. 63 (1998) 5228-5231.

[3] P. von Ragué Schleyer, H. Jiao, N. van Eikema Hommes, V. Malkin, O. Malkina, J. Am. Chem. Soc. 119 (1997) 12669-12670.

[4] Z. Chen, C.S. Wannere, C. Corminboeuf, R. Puchta, P.v.R. Schleyer, Chem. Rev. 105 (2005) 3842-3888.

[5] J.O.C. Jiménez-Halla, E. Matito, J. Robles, M. Solà, J. Organometall. Chem. 691 (2006) 4359-4366.

[6] A. Stanger, J. Org. Chem. 71 (2006) 883-893.

[7] P.v.R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N.J.v.E. Hommes, J. Am. Chem. Soc. 118 (1996) 6317-6318.

[8] R. Gershoni-Poranne, C.M. Gibson, P.W. Fowler, A. Stanger, J. Org. Chem. 78 (2013) 7544-7553.

[9] T. Krygowski, M. Cyranski, Z. Czarnocki, G. Häfelinger, A.R. Katritzky, Tetrahedron, 56 (2000) 1783-1796.

[10] N.S. Mills, K.B. Llagostera, J. Org. Chem. 72 (2007) 9163-9169.

[11] W.E. Barth, R.G. Lawton, J. Am. Chem. Soc. 88 (1966) 380-381.

[12] A.Y. Rogachev, A.S. Filatov, A.V. Zabula, M.A. Petrukhina, Phys. Chem. Chem. Phys. 14 (2012) 3554-3567.

[13] M.V. Frash, A.C. Hopkinson, D.K. Bohme, J. Am. Chem. Soc. 123 (2001) 6687-6695.

[14] P.A. Denis, J. Mol. Struct. THEOCHEM, 865 (2008) 8-13.

[15] M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, J. Montgomery Jr, T. Vreven, K. Kudin, J. Burant, J. Millam, S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, Cossi M, G. Scalmani, N. Rega, G. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. Knox, H. Hratchian, J. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. Stratmann, O. Yazyev, A. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Ayala, K. Morokuma, G. Voth, P. Salvador, J. Dannenberg, V. Zakrzewski, S. Dapprich, A. Daniels, M. Strain, O. Farkas, D. Malick, A. Rabuck, K. Raghavachari, J. Foresman, J. Ortiz, Q. Cui, A. Baboul, S. Clifford, J. Cioslowski, B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Martin, D. Fox, T. Keith, M. Al-Laham, C. Peng, A. Nanayakkara, M. Challacombe, P. Gill, B. Johnson, W. Chen, M. Wong, C. Gonzalez, J. Pople, Gaussian 03, Revision E. 01. Wallingford CT: Gaussian, Inc.(http://www. gaussian. com), (2004)

[16] A. Frisch, H. Hratchian, R. Dennington, A. Todd, T. Keith, J. Millam, GaussView 5, 2009.

[17] K. Wolinski, J.F. Hinton, P. Pulay, J. Am. Chem. Soc. 112 (1990) 8251-8260.

[18] K. Kavitha, M. Manoharan, P. Venuvanalingam, J. Org. Chem. 70 (2005) 2528-2536.