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INVESTIGATION OF AROMATICITY OF TRI AND TETRAAZANAPHTHALENE DERIVATIVES

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Abstract

Aromaticity of a compound gives important information about the possible reactions and other propeties of a molecule. In that point of view measurement of aromaticity is very important. Although there are a few applications for the determination of aromaticity, Nucleus Independent Chemical Shift calculations provide the easiest computation and best approach to the result. Naphthalene is an aromatic molecule with two fused benzene rings. It is clear that centric replacement of carbons with heteroatoms will affect the aromaticity of naphthalene. Substitution of parent carbon atoms of the ring with electronegative nitrogen atoms will decrease the aromaticity of the system. The positions of the nitrogens should also effect the aromaticity of the total system. Therefore, this work was formed by taking all the derivatives of tri and *tetraazanaphthalene derivatives into consideration. In order to gain the lost aromaticity due to nitrogen substitution, ring hydrogens were substituted with electron withdrawing nitro groups.*

Keywords

Aromaticity, Nucleus Independent Chemical Shift, Tetraazanaphthalene, Triazanaphthalene

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1. Introduction

Naphthalene is composed of two fused benzenes, and it has been studied frequently with its derivatives for about fifty years, since 1968 (Yencha & El-Sayed, 1968; Kitagawa, 1968; Kaim, Tesmann & Bock, 1980; Klasinc, Kovac & Gusten, 1983; Meylan & Howard, 1991; Heinis, Chowdhury & Kebarle, 1993; Schiedt, Knott, Barbu, Schlag & Weinkauf, 2000; Lardin, Squires & Wenthold, 2001; Song, et al. 2002). Ghiasi (Ghiasi, 2005) worked on the aromaticity of mono- and di-silanaphthalene after the first achievement of the synthesis of 1-Silanaphthalene was published by Takeda et al. (Takeda, Shinohara & Tokitoh, 2002). Azanaphthalenes have attracted the attention of the scientists in terms of its synthesis and theoretical properties due to their importance in certain biological reactions (Brogli, Heilbronner & Kobayashi, 1972; Meot-Ner, Liebman & Kafafi, 1988; Schafer, Schweig, Markl & Heier, 1973; Schafer, Schweig, Vermeer, Bickelhaupt & Graaf, 1975; Wang & Wang, 2007; Spedaletti, et al. 2005). The aromaticity of substituted azabenzenes and azanaphthalines have been studied recently (Gümüş, 2011; Gümüş, 2011).

Naphthalene is isoelectronic with Cinnoline, quinazoline, phthalazine and quinoxaline which are famous heteroaromatic compounds. The main aim of the current work is to investigate the effect of substitution on the ground state geometry, stability and the aromaticity of all possible tri and tetraaza derivatives of naphthalene.

Aromaticity has still been considered as an actively investigated area of chemistry. There are a few criterion for monocyclic compounds to be promoted as aromatic; they possess uncut conjugation in the main circle with the proper number of π-electrons (i.e., the Hückel rule). While this criteria work sufficiently to predict the aromaticity of neutral and charged ring systems, it cannot be an obvious indicator of aromaticity for more complex structures.

Aromaticity is described by a combination of properties in cyclic conjugated compounds. Generally, aromaticity has been expressed in terms of energetic, structural and magnetic criteria (Minkin, Glukhovtsev & Simkin, 1994; Schleyer & Jiao, 1996; Glukhovtsev, 1997; Krygowski, Cyranski, Czarnocki, Hafelinger & Katritzky, 2000; Schleyer, 2001; Cyranski, Krygowski, Katritzky & Schleyer, 2002). In 1996, Schleyer introduced an easy but an efficient way for definition aromaticity: Nucleus-independent chemical shift (NICS) (Schleyer, Maerker, Dransfeld, Jiao & Hommes, 1996), which is the calculated value of the negative magnetic shielding at some selected point in space, usually, at center of a ring or cage. Negative NICS data indicate aromaticity (-11.4 for naphthalene) and positive NICS data mean antiaromaticity (28.8 for cyclobutadiene) while small values of NICS are accepted as an indicator for nonaromaticity (-3.1 for 1,3-cyclopentadiene). NICS might be a useful indicator of aromaticity that often correlates well with the other energetic, structural and magnetic criteria for aromaticity (Jiao & Schleyer, 1998; Schleyer, Kiran, Simion & Sorensen, 2000; Quinonero, et al. 2002; Patchkovskii & Thiel, 2002). Resonance energies and magnetic susceptibilities can be used to define the overall aromaticity of a polycyclic compound, but do not provide information about the individual rings. However, NICS is an effective probe for local aromaticity of separate rings of polycycles.

In order to enlighten the effect of aza substitution on the naphthaline skeleton, we have applied NICS calculations using Density Functional Theory. The computed energies and the NICS values have been used to compare the stabilities of the structures.

2. Method of Calculation

The ground state optimizations of naphthalene derivatives leading to minimum energy geometry were achieved by using MM2 method followed by semi-empirical PM3 self-consistent field molecular orbital (SCF MO) method (Stewart, 1989; Stewart, 1989) at the restricted level (Leach, 1997). Then, further optimizations were done within the application of density functional theory (DFT, B3LYP) (Kohn & Sham, 1965; Parr & Yang, 1989) at the level of 6-31G(d,p) (restricted closed-shell) (Stewart, 1989). The hybrid functional term of B3LYP is a combination of hybrid Hartree–Fock and local spin density (LSD) exchange functions with Becke’s gradient correlation to LSD exchange (Becke, 1988). B3LYP is formed by Vosko, Wilk, Nusair (VWN3) local correlation functional (Vosko, Vilk & Nusair, 1980) and Lee, Yang, Parr (LYP) correlation correction functional (Lee, Yang & Parr, 1988). The BLYP method shows a better improvement over the SCF-HF results. Its predictions are in quite good agreement with experiment (Scuseria, 1992; Sosa & Lee, 1993; Wilson, Amos & Handy, 2000).

The normal mode analysis for each structure did not yield any imaginary frequencies for the 3N-6 vibrational degrees of freedom, where N is the number of points in the system. This shows that the structure of each optimized structure corresponds to at least a local minimum on the potential energy surface.

Absolute NMR shielding values (Pulay, Hinton & Wolinski, 1993) were computed using the Gauge-Independent Atomic Orbital method (Hehre, Radom, Schleyer & Pople, 1986) with the restricted closed shell formalism applying 6-31G(d,p) basis set over B3LYP/6-31G(d,p) geometry optimized structures. NICS values were obtained by calculating absolute NMR shielding at the ring centers, NICS(0).

The ground state geometry optimizations and NICS computations of all the compounds have been performed by the use of Gaussian 09 package program (Frisch et al., 2010).

3. Results and Discussion

Investigation of the effect of centric replacement of an heteroatom to the main sceleton, and/or an heteroatom or heterogroup substitution of the hydrogens connected to the parent circle of well-known aromatic compounds has been attractive scientists for both theoretical and experimental studies. In this work, all possible tri and tetraazanaphthalene derivatives and their susbtituted (NO_2) counterparts have been taken into consideration theoretically by the application of B3LYP/6-31G(d,p) level of theory in order to judge their ground state stabilities and aromaticities. The aza replacement on positions 9 and 10 are totally excluded since, we end up with nonaromatic derivatives in these cases.

The first step of the current study was obtaining the ground state geometries of all the compounds using B3LYP/6-31G(d,p) level of theory. The geometry optimized structures of triazanaphthalenes and tetraazanaphthalenes can be seen in Figure 2 and Figure 3, respectively. The numbers in the naming of the compounds indicate the positions of nitrogen substitution.

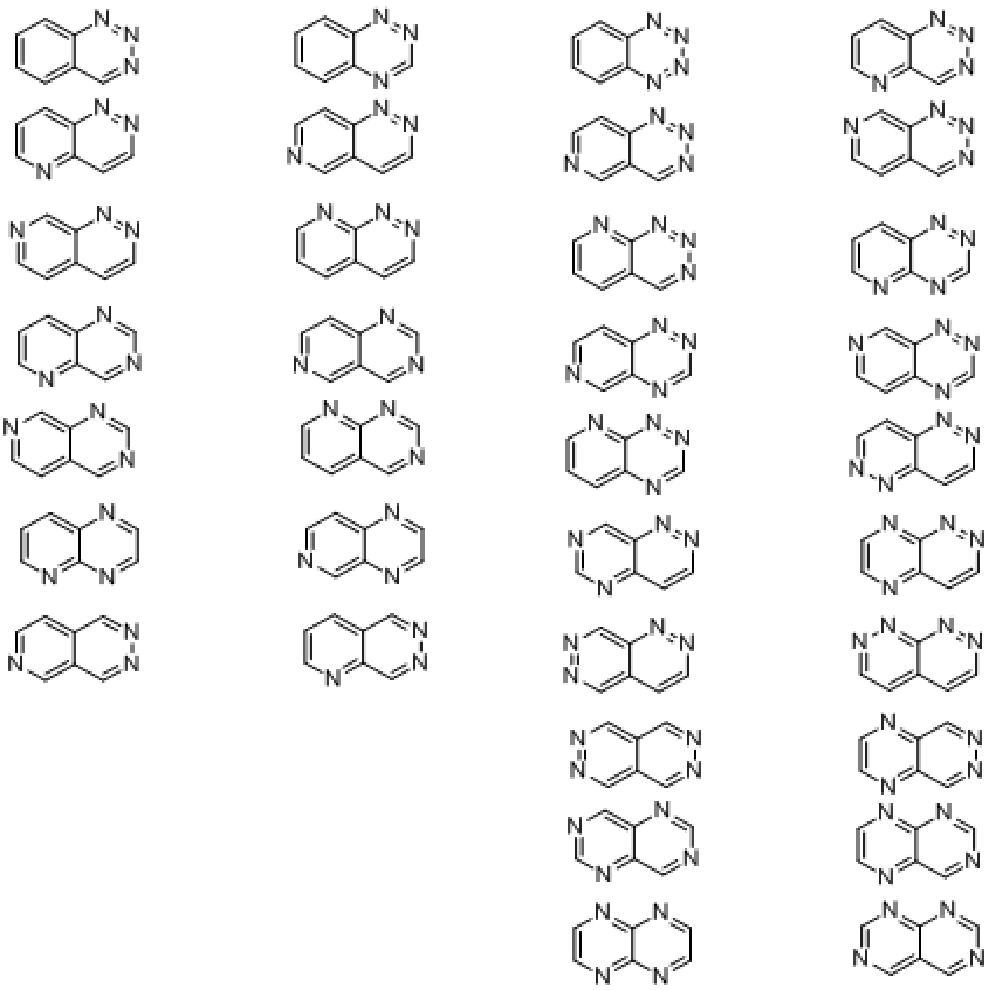

Figure 1: *The structures of the tri and derivatives considered in the present study*

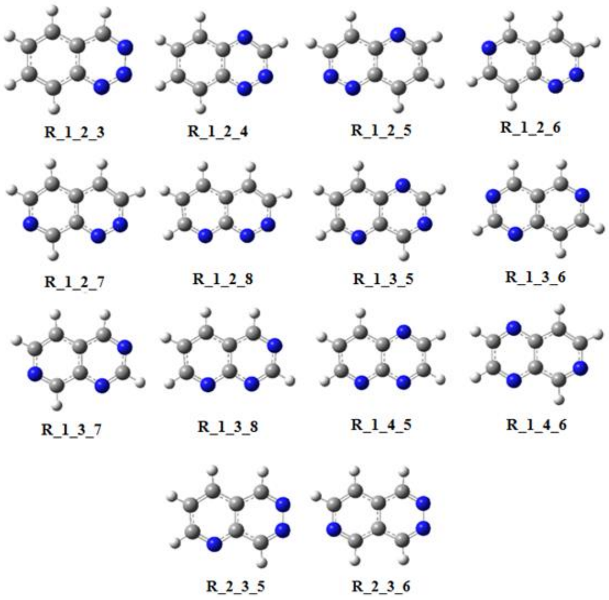

Figure 2: *The geometry optimized structures of the triazanaphthalene derivatives*

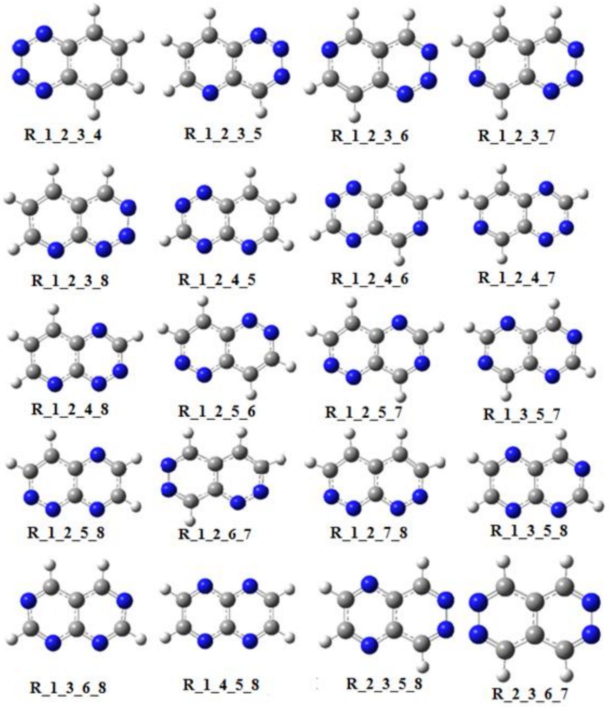

Figure 3: *The geometry optimized structures of the tetraazanaphthalenes*

Insersion of heteroatoms into the structures of aromatic systems will surely effect the stabilities of the molecules negatively due to loss of perfect delocalization throughout the π system. The aromaticity of the system will be disturbed as a result of centric substitution. Moreover, the positions of the nitrogens in either rings of the parent naphthalene structure may have different effects on the stablity. Total energies obtained upon geometry optimizations have been tabulated in Table 1 for all the heteroatom substituted systems. The energetics of the cmpounds have also been drawn on a graph in order to be able to better observe the change of stability with the positions of nitrogens (Figure 3 and Figure 4).

Table 1: *Total energies (Hartree) of the nitrogen substituted naphthalene derivatives*

Compound	**Energy**		**Compound**	**Energy**
R_1_2_3	-433.9677225		**R_1_2_3_4**	-449.9721622
R_1_2_4	-433.9926668		**R_1_2_3_5**	-450.0008531
R_1_2_5	-433.9926668		**R_1_2_3_6**	-449.9968602
R_1_2_6	-433.9880903		**R_1_2_3_7**	-449.9963041
R_1_2_7	-433.9883967		**R_1_2_3_8**	-449.9978227
R_1_2_8	-433.9881091		**R_1_2_4_5**	-450.0261427
R_1_3_5	-434.0255308		**R_1_2_4_6**	-450.0216086
R_1_3_6	-434.0270475		**R_1_2_4_7**	-450.0230118
R_1_3_7	-434.0250151		**R_1_2_4_8**	-450.0240463
R_1_3_8	-434.0278608		**R_1_2_5_6**	-449.9884115
R_1_4_5	-434.0237988		**R_1_2_5_7**	-450.0266519
R_1_4_6	-434.0216474		**R_1_2_5_8**	-450.0198953
R_2_3_5	-433.9924697		**R_1_2_6_7**	-449.9882265
R_2_3_6	-433.9895173		**R_1_2_7_8**	-449.9835240
			R_1_3_5_7	-450.0623512
			R_1_3_5_8	-450.0586271
			R_1_3_6_8	-450.0632366
			R_1_4_5_8	-450.0539892
			R_2_3_5_8	-450.0218515
			R_2_3_6_7	-449.9884963

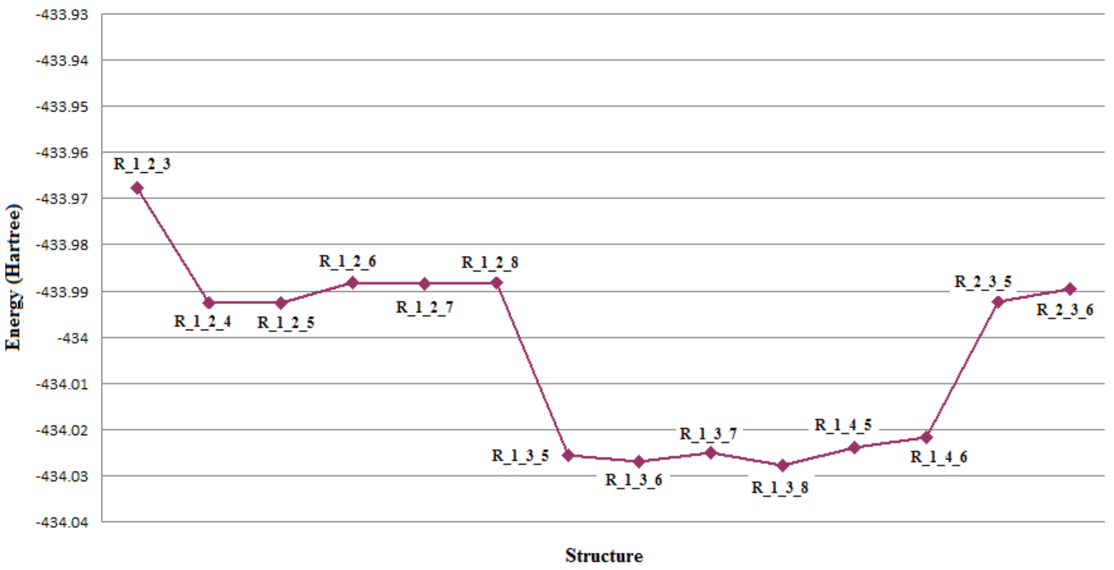

Figure 4: *Stabilities of triazanaphthalenes*

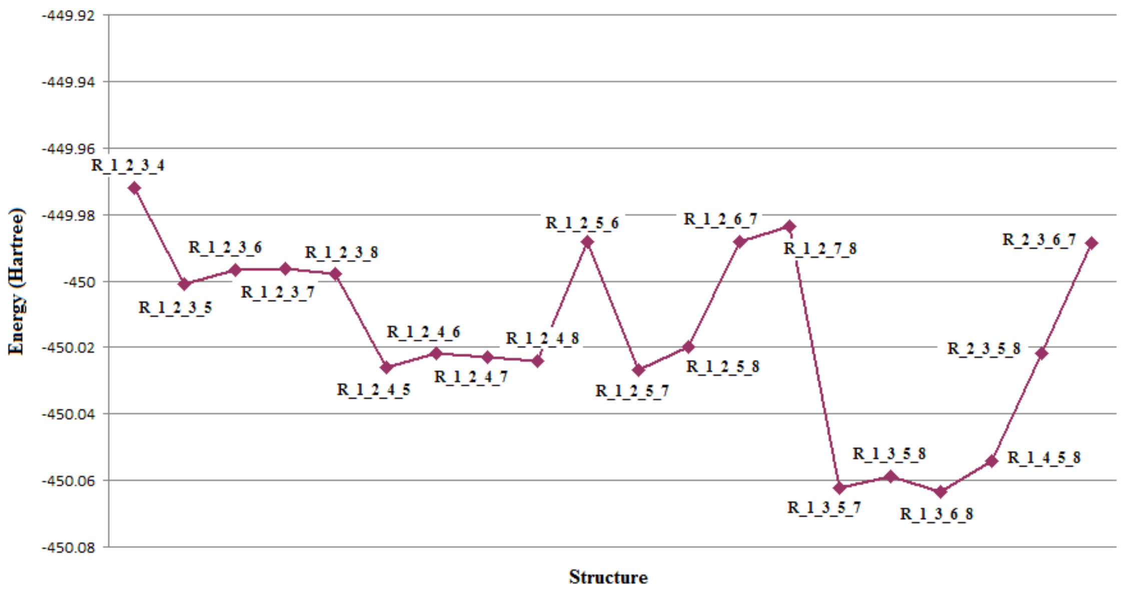

Figure 5: *Stabilities of tetraazanaphthalenes*

Figure 4 and Figure 5 show the stabilities of triazanaphthalene and tetraazanaphthalene derivatives, respectively. The bigger the number of nitrogens in one of the rings the more unstable the system. Therefore, **R_1_2_3** and **R_1_2_3_4** have been found to be least stable ground state structures. On the other hand, the structures where nitrogens spread all over the molecule are more stable. These results are not surprising since the electronwithdrawing nitrogen atoms pull the electrons of the π-system towards themselves reducing the aromaticity. **R_1_3_8** and **R_1_3_6_8** have been computed to be the most stable molecules. In these cases nitrogen atoms are located far from each other, which leads a symmetrical distribution of π-electrons thus, a better conjugation achieved.

After geometry optimizations, the aromaticities of the compounds were calculated by the applications of NICS calculations. NICS data can be obtained by computing the NMR of the systems on the center of the ring. There aren't any real atoms at the center of the rings however, magnetic shielding at any point at the space can be measured by introducing dummy atoms to the system. In Figure 6, an illustration of NICS calculations has been shown. The ring hand ring was named as the A ring and visa versa the left ring is called as the B ring. The results of the NICS calculations have been tabulated in Table 2 and Table 3. The NICS data for naphthalene itself is -11.4 ppm for each ring. The values in these tables indicate that substitution of nitrogen to either rings of naphthalene drastically decreases the aromaticity of that ring. When nitrogens are located in the same ring (**R_1_2_3** and **R_1_2_3_4**), NICS data decrease down to -5.29 ppm and -4.23 ppm, respectively. For the derivatives where nitrogen atoms spread all over the molecule the NICS values have been computed to be higher but still lower than naphthalene due to disturbed aromaticity. For the cases of two nitrogens located in Ring A, the aromaticiy of the system is higher when nitrogen are located close to each other. For example **R_1_2_5** and **R_1_3_5** have NICS data of -7.17 and -5.42 ppm, respectively. That is due to the fact that close nitrogens loose the ability to withdraw electrons from the π system, thus, the delocalization is less disturbed.

If aromaticity was a summable property, napthalene would have a total aromaticity of -22.8 ppm magnitute. The same argument has been applied for the present systems and total aromaticies have been given in Table 2 and Table 3 as a third column. As expected total aromaticity data were decreased upon nitrogen substitution. However, it was nice to observe that total aromaticities are found to be nearly the same throughout the series. The total aromaticity data for triazanaphthalenes are greater that that of tetraazanaphthalenes which indicate our argument of total aromaticity is applicable.

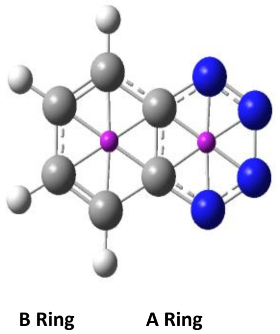

Figure 6: *Illustration for NICS calculation*

Table 2: *NICS data for triazanaphthalene derivatives (ppm)*

Structue	**A Ring**	**B Ring**	**Total**
R_1_2_3	-5.29	-9.46	-14.75
R_1_2_4	-5.51	-9.11	-14.62
R_1_2_5	-7.17	-7.54	-14.71
R_1_2_6	-6.94	-8.00	-14.94
R_1_2_7	-6.79	-7.39	-14.18
R_1_2_8	-7.07	-7.95	-15.02
R_1_3_5	-5.42	-7.07	-12.49
R_1_3_6	-6.32	-7.81	-14.13
R_1_3_7	-6.63	-7.88	-14.51
R_1_3_8	-6.86	-7.82	-14.68
R_1_4_5	-6.46	-7.94	-14.40
R_1_4_6	-6.12	-7.86	-13.98
R_2_3_5	-5.73	-7.95	-13.68
R_2_3_6	-5.71	-8.21	-13.92

Table 3: *NICS data for tetraazanaphthalene derivatives (ppm)*

Structue	**A Ring**	**B Ring**	**Total**
R_1_2_3_4	-4.23	-9.07	-13.30
R_1_2_3_5	-5.27	-8.09	-13.36
R_1_2_3_6	-5.24	-8.34	-13.58
R_1_2_3_7	-6.28	-7.82	-14.10
R_1_2_3_8	-5.43	-8.42	-13.85
R_1_2_4_5	-5.77	-7.97	-13.74
R_1_2_4_6	-5.51	-8.32	-13.83
R_1_2_4_7	-5.31	-7.91	-13.22
R_1_2_4_8	-5.61	-8.24	-13.85
R_1_2_5_6	-7.39	-7.40	-14.79

R_1_2_5_7	-7.24	-6.36	-13.60
R_1_2_5_8	-7.39	-6.38	-13.77
R_1_2_6_7	-7.31	-5.67	-12.98
R_1_2_7_8	-7.27	-7.19	-14.46
R_1_3_5_7	-6.63	-6.69	-13.32
R_1_3_5_8	-6.36	-6.78	-13.14
R_1_3_6_8	-6.73	-6.75	-13.48
R_1_4_5_8	-6.71	-6.69	-13.40
R_2_3_5_8	-5.85	-6.42	-12.27
R_2_3_6_7	-6.25	-6.29	-12.54

The next step of the project was to answer; Is it possible to regain the lost aromaticity? We thought that susbtitution of hydrogen remained with a good electron withdrawing group may pull the electrons located on electronegative nitrogens towards the carbon atom and thus, to the ring current. What we expected has been proven by the computations. The geometry optimized groud state sructures as well as the aromaticity of nitro substituted triazanaphthalene derivatives can be seen in Figure 7. **R_1_2_3** has been found to possess -5.30 ppm NICS value on the ring A before nitro substitution and the aromaticity of the ring A has been enhanced up to -6.31 ppm after nitro substitution. The same procedure has been applied for **R_1_2_4** and NICS value was calculated to increase from -5.51 to -7.07 ppm. Moreover, the effect of position of nitro substitution has been tested over **R_1_2_5**. Nitro group could be located on position 3 or position 4. The results of the computations showed that the electron withdrawing ability of nitro group is better valid when it is closer to the nitrogens. Although the aromaticity of the parent naphthalene system has been improved in both cases from -7.18 ppm to -7.62 (nitro at position 4) and -8.23 ppm (nitro at position 3), it was proven that the closer nitro group to the nitrogens the better the aromatcity of the system.

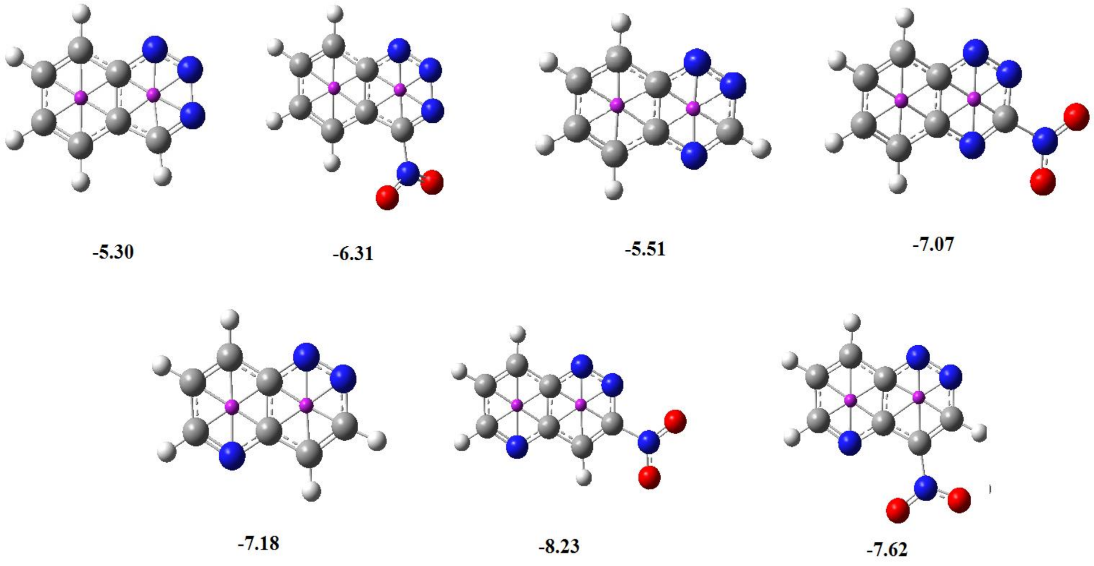
-5.30 -6.31 -5.51 -7.07
-7.18 -8.23 -7.62

Figure 7: *Geometry optimized structures and calculated NICS (ppm) data for NO_2 substituted triazanaphthalene derivatives*

4. Conclusion

The general objective of the paper was to investigate the effect of aza substitution on the aromaticity of tri and tetraazasubstituted naphthalene derivatives via computation of Nucleus Independent Chemical Shift (NICS) data.

Energy data showed that the closer the nitrogens to each other, the less stable the compound. Similar argument also holds for NICS calculations. NICS data get smaller for derivatives where nitrogens are located closely. Aza substitution to parent naphthalene decreased the aromaticity of the present compounds. On the other hand, the lost aromaticity could be gained back upon insertion of nitro group acting as a very strong electron withdrawing group.

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