The Aromaticity of Diamino-Dinitro-Diaza-Benzenes

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Abstract: The aromaticities of all possible dinitro, diamino substituted diaza derivatives of benzene; pyrazine, pyrimidine and pyridazine, have been investigated by computational calculations at the level of B3LYP/6-31G(d,p). The NICS (0), NICS (0.5), NICS (1.0) data have been reported herein. **2_5,6A_2,4N** and **3_2,3A_5,6N** are found to be the most aromatic structures among all. The results indicated that, the more closer the nitro groups to the aza points, the more aromatic the structure.

Keywords: Aromaticity, NICS, pyridazine, pyrimidine, pyrazine

Introduction

In organic chemistry, the structures of some rings of atoms are unexpectedly stable. Aromaticity is a chemical property in which a conjugated ring of unsaturated bonds, lone pairs, or empty orbitals exhibit a stabilization stronger than would be expected by the stabilization of conjugation alone. It can also be considered a manifestation of cyclic delocalization and of resonance [1-3].

This is usually considered to be because electrons are free to cycle around circular arrangements of atoms which are alternately single- and double-bonded to one another. These bonds may be seen as a hybrid of a single bond and a double bond, each bond in the ring identical to every other. This commonly-seen model of aromatic rings, namely the idea that benzene was formed from a six-membered carbon ring with alternating single and double bonds (cyclohexatriene), was developed by Kekulé. The model for benzene consists of two resonance forms, which corresponds to the double and single bonds superimposing to give rise to six one-and-a-half bonds. Benzene is a more stable molecule than would be expected without accounting for charge delocalization.

Pyridazine (1,2-diazabenzene), pyrimidine (1,3-diazabenzene) and pyrazine (1,4-diazabenzene) are diaza analogs of benzene. They are isoelectronic with benzene by containing 6π electrons for aromatic delocalization. However, the perfect aromaticity of benzene has been disturbed by diaza perturbation in the case of the systems under consideration such that, the electronegative nitrogens hold some of the ring electrons to prevent perfect delocalization of the 6π electrons.

Method of Calculation

All systems were investigated by using the hybrid functional B3LYP as implemented in the Gaussian 03 package [4].

The normal mode analysis for each structure yielded no imaginary frequencies for the $3N-6$ vibrational degrees of freedom, where N is the number of atoms in the system. This indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface.

Absolute NMR shielding values [5] were calculated using the Gauge-Independent Atomic Orbital method [6] with the restricted closed shell formalism employing 6-

31G(d,p) basis set over B3LYP/6-31G(d,p) optimized geometries. NICS values were obtained by calculating absolute NMR shielding at the ring centers NICS(0), 0.5 Å NICS(0.5) and 1.0 Å NICS(1.0) above the center of the ring, respectively .

Results and Discussion

The present work deals with the aromaticities of diaza analogs of benzene and their diamino, dinitro substituted derivatives. The idea of amino and nitro substitution on pyridazine, pyrimidine and pyrazine arised from the fact that the aromaticity of these rings could be increased by substitution of electron donating groups together with electron withdrawing groups. The latter must be closer to the diaza points so that the ring electrons located on the electronegative nitrogens can be pulled back into the ring to augment the π electron cloud of the ring as well as the aromaticity. The structures of the systems investigated herein can be seen in Figure 1.
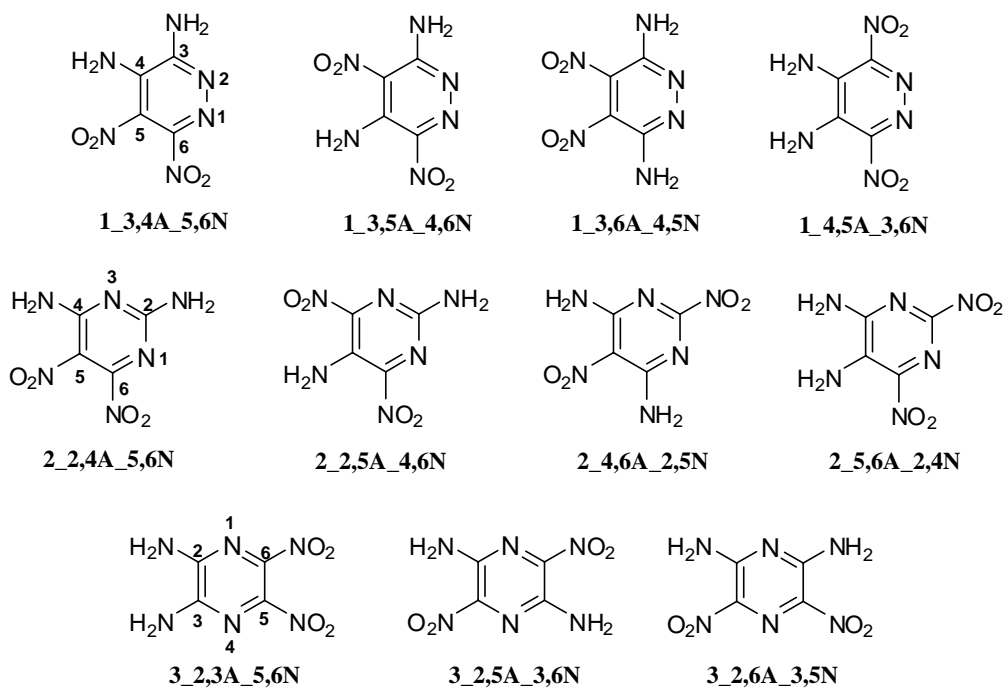

Figure 1. The structures and naming of the systems studied.

Aromaticity is expressed by a combination of properties in cyclic delocalized systems. In general, aromaticity is discussed in terms of energetic, structural and magnetic criteria [7-12]. In 1996, Schleyer has introduced a simple and efficient probe for aromaticity: Nucleus-independent chemical shift (NICS) [13], which is the computed value of the negative magnetic shielding at some selected point in space, generally, at a ring or cage center. Negative NICS values denote aromaticity (-11.5 for benzene, -11.4 for naphthalene) and positive NICS values denote antiaromaticity (28.8 for cyclobutadiene) while small NICS values indicate non-aromaticity (-3.1 for 1,3-cyclopentadiene). NICS may be a useful indicator of aromaticity that usually correlates well with the other energetic, structural and magnetic criteria for aromaticity [14-17]. Resonance energies and magnetic susceptibilities are measures of the overall aromaticity of a polycycle, but do not provide information about the individual rings. However, NICS is an effective probe for local aromaticity of individual rings of polycyclic systems.

Table 1 Calculated NICS (ppm) data for the present systems.

System	NICS (0)	NICS (0.5)	NICS (1.0)
Pyridazine	-5.8	-7.7	-7.3
1_3,4A_5,6N	-7.5	-9.5	-9.1
1_3,5A_4,6N	-4.2	-6.1	-5.9
1_3,6A_4,5N	-6.4	-8.3	-8.1
1_4,5A_3,6N	-8.4	-10.2	-9.8
Pyrimidine	-6.5	-8.6	-7.9
2_2,4A_5,6N	-5.3	-7.1	-6.6
2_2,5A_4,6N	-8.0	-9.9	-9.7
2_4,6A_2,5N	-5.6	-7.3	-7.1
2_5,6A_2,4N	-9.1	-11.3	-11.0
Pyrazine	-6.3	-8.1	-8.0
3_2,3A_5,6N	-9.0	-11.1	-10.7
3_2,5A_3,6N	-8.0	-10.1	-9.8
3_2,6A_3,5N	-5.5	-7.7	-7.3

The calculated NICS data for the present systems together with the unsubstituted analogs are given in Table 1. The data reveals that **2_5,6A_2,4N** and **3_2,3A_5,6N** are the most aromatic structures among all. By the inspection of the data in Table 1, the effect nitro groups closer to the aza substitution points can be observed clearly. The most aromatic systems of each series are the ones where nitro groups are situated on the closest distance to the aza points; **1_4,5A_3,6N**, **2_5,6A_2,4N** and **3_2,3A_5,6N** for each pyridazine, pyrimidine and pyrazine series, respectively. The reverse is also observed by the NICS data, when the strongly electron withdrawing nitro groups are away from the aza points, the aromaticity decreases even lower from the unsubstituted counterpart.

Acknowledgements

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