Journal of Molecular Structure: THEOCHEM 822 (2007) 33–37

THEO CHEM

www.elsevier.com/locate/theochem

Relation between the substituent effect and aromaticity in tetrazoles, protonated tetrazoles and tetrazolate derivatives

Alireza Najafi Chermahini [a,*], Hossein Abdol Dabbagh [b], Abbas Teimouri [c]

[a] *Department of Chemistry, Faculty of Science, Yasouj University, Yasouj, Iran*
[b] *Department of Chemistry, Isfahan University of Technology, Isfahan, Iran*
[c] *Payame Noor University, Isfahan, Iran*

Received 16 June 2007; received in revised form 16 July 2007; accepted 18 July 2007
Available online 25 July 2007

Abstract

The energies, geometries and aromaticity of a series of 5R tetrazoles [R = NH_2, OH, OCH_3, SCH_3, H, CH_3, F, Cl, BH_2, CF_3, CN, NO, NO_2], their anions and protonated forms in the gas phase have been calculated with the DFT/B3LYP method at the 6-31++G** level. We have analyzed the change of local aromaticity by NICS and HOMA and found a considerable ring aromaticity by tetrazole and tetrazolate anions and their protonated forms. In analysis by NICS, anion forms have the least aromaticity and in neutral forms 1-H tetrazoles have less aromaticity character than 2-H ones. Interestingly among of protonated forms 2,3-H forms have the most aromaticity character and others follow: 1,2-H > 1,3-H > 1,4-H. However, analysis by HOMA index showed that aromaticity is related to nature of groups at the 5 position. The protonated form of 1,4-H tetrazoles have the least aromaticity character.

Keywords: Aromaticity; NICS; HOMA index; Tetrazole; Tetrazolate; Protonated tetrazoles; DFT

---

1. Introduction

Aromaticity is one of the cornerstones of modern organic chemistry [1,2]. It fundamentally characterizes the molecular structure, physical properties and chemical reactivity from both thermodynamic and kinetic standpoints [1–6]. The aromaticity was used as a very powerful predictive tool for compounds that have not been prepared previously. Therefore, it is significant in any logical applications of organic chemistry. Several different quantitative criteria of aromaticity based on (i) energetic stabilization of cyclic p-systems (resonance energy), (ii) magnetic properties caused by ring currents and (iii) structural properties (bond equalization) were suggested [2,3,7–10]. During the last decade, the most popular approaches for characterizing the degree of aromaticity are based on structural and magnetic properties of aromatic systems. In particular, Bird [11] and Pozharsky [12] indices apply with bond lengths and bond orders derived from experimental or theoretical data. Aromaticity supposes full equalization of these values within the benzene ring. Therefore, the degree of deviation of distribution of bond lengths and bond orders within carbocycle from uniform may be used for the measurement of aromaticity. Much more reliable is another aromaticity index, harmonic oscillator model of aromaticity (HOMA) approach [13,14] extended later into heteroatomic systems [15] and applied for investigations of many aromatic and heteroaromatic systems [8,9,16]. The measurements of magnetic properties have led to the quantities approach to aromaticity based on exaltation and anisotropy of magnetic susceptibility [7,10]. The recent development of reliable quantum-chemical methods of calculations of magnetic properties of organic molecules has resulted in the development of efficient method for estimating the degree of aromaticity based on calculations of nuclear independent chemical shifts at the center of the

---

[*] Corresponding author. Tel./fax: +98 7412223048.
E-mail addresses: najafi@mail.yu.ac.ir, najafy@gmail.com (A. Najafi Chermahini).

0166-1280/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.theochem.2007.07.012

aromatic ring (NICS0) or 1 Å above the center of the ring (NICS1) [17,18]. This approach has been successfully applied to various monocyclic aromatic systems including large annulenes [7,19,20].

Tetrazoles are a class of heterocycles with a wide range of applications that is receiving considerable attention [21]. Recently aromaticity of tetrazole derivatives investigated by Trifonov and coworkers [22], they conclude that the most aromatic tetrazoles are the tetrazolate anions and the forms containing proton in the position 2. In the present paper, we investigate relation between substituent and aromaticity in tetrazole derivatives by NICS and HOMA methods.

2. Computational method

The geometries of the compounds studied were optimized at the B3LYP/6-31++G(d,p) density functional levels without any geometrical restrictions with the GAUSSIAN 98 program package [23]. The nature of each stationary point was characterized by computing the harmonic vibrational frequencies at the same level of theory. Besides, Gauge invariant atomic orbitals (GIAO) method was applied to estimate the magnetic tensor shielding within the same level of approximation (GIAO-B3LYP/6-31++G** //B3LYP/6-31++G(d,p)) [24]. The ghost atoms used in this procedure were placed in the center and 1 Å above the five-member ring. Generally, a negative NICS value denotes aromaticity and a positive value shows anti-aromaticity. And NICS value fluctuating around zero indicates nonaromaticity.

The harmonic oscillator model of aromaticity (HOMA) is calculated as follows:

$$\mathrm{HOMA} = 1 - \frac{1}{n}\sum \alpha(R_{\mathrm{opt}} - R_{\mathrm{i}})^2,$$

where n stands for number of all bonds, α is normalization factor preserving HOMA = 0 for hypothetical Kekule structure and HOMA = 1 for perfect aromatic compound. The values of R_{opt} and α values were obtained for many types of bonds [6,14]. For example carbon–carbon bond is characterized by $R_{\mathrm{opt}} = 1.397$ Å and $\alpha = 257.7$, but for nitrogen–carbon and nitrogen–nitrogen bonds $R_{\mathrm{opt}} =$ 1.334 and 1.309 Å, respectively, and $\alpha = 93.52$ [14], these data were used in this study for all tetrazole derivatives.

3. Results and discussion

3.1. Energies and stabilities

The DFT calculated gas phase energies for the tetrazoles and their corresponding anions, relative stability of tetrazoles, deprotonation energies and dipole moments of tetrazole derivatives are given in Table 1. It is well known that in the gas phase, 2-H tautomer in tetrazoles are more stable than 1-H forms [25–28]. Table 1 shows that for all substituted tetrazoles, the 2-H forms are 0.9–5.08 kcal/mol more stable with regard to 1-H tautomer. In addition, the mean value ΔE is substantially greater for electron withdrawing groups (NO_2, NO, CN) than for electron releasing ones (OH, NH_2, OCH_3). Besides, the effect of the substituents on the relative stability of tautomers is insignificant and does not show a regular trend. Our data are in good agreement with the previously known ones of theoretical calculations for the unsubstituted tetrazole and some of its 5R-derivatives [22,26–29]. Previously it

Table 1
Total energies, relative stabilities, dissociation energies and dipole moment of tetrazole derivatives

R	Neutral tetrazoles					Anion		
	E_{Total}		$E_2 - E_1$[b]	μ[c]		E_{Total}	$E^{-}_{\mathrm{Tet}} - E_{\mathrm{Tet\text{-}H}}$	
	1-H	2-H		1-H	2-H		1-H	2-H
NO_2	−462.7551728[a]	−462.7594862[a]	−2.71	3.40	5.10	−462.2572551[a]	312.44	315.15
NO	−387.5458843	−387.5517983	−3.71	4.07	4.42	−387.0436252	315.17	318.88
CN	−350.4993726	−350.5053841	−3.77	3.78	4.95	−349.9977668	314.76	318.53
CF_3	−595.3157516	−595.3213875	−3.54	4.00	3.79	−594.8058903	319.94	323.47
BH_2	−283.7139092	−283.7156227	−1.08	4.83	2.67	−283.1886077	329.63	330.70
F	−357.4966029	−357.5047004	−5.08	4.61	3.10	−356.9778228	325.53	330.62
Cl	−717.853694	−717.8591515	−3.42	4.83	2.80	−717.3345118	325.79	329.20
H	−258.2681382	−258.2726229	−2.80	5.56	2.32	−257.7329820	335.81	338.62
CH_3	−297.5966027	−297.6004571	−2.41	6.02	2.17	−297.0564118	338.97	341.39
SCH_3	−695.7713553	−695.7786356	−4.57	7.05	0.60	−695.2436370	331.14	335.71
OCH_3	−372.8024955	−372.8039305	−0.90	5.11	0.39	−372.2631148	338.46	339.36
SH	−656.455821	−656.4599214	−2.57	4.74	1.47	−655.9281188	331.13	333.71
OH	−333.4972609	−333.500242	−1.87	4.64	0.94	−332.9618167	335.99	337.86
NH_2	−313.6357186	−313.6413611	−3.54	6.41	2.40	−313.0956512	338.89	342.43

[a] Total energies in Hartree.
[b] kcal mol^{-1}.
[c] Debye.