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Theoretical Investigation on the Aromaticity of Mono-Substituted Benzene Derivatives by Using Cyclic Reference

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Abstract

The degree of aromaticity of mono-substituted derivatives of benzene has been investigated using a new index based on electric field gradient index, by using two mechanical quantum methods with Gaussian 03. Two different basis sets have applied to study and the results compared. This strategy has demonstrated that, due to violation of symmetry in have pi-systems, how the degree of aromaticity can have been changed. A comparison of the values of our aromaticity index with other indices reveals a good correlation for these compounds

Keywords: Mono-substituted benzene, Electrostatic Field Gradient, EFG, Aromaticity

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 [7].

A considerable broad range of cyclic organic molecules containing conjugated systems requires reliable approaches for estimation of aromaticity. A more detailed investigation of aromatic molecules requires a quantitative estimation of the degree of aromaticity of cyclic conjugated systems. Therefore, several different quantitative criteria of aromaticity based on (i) energetic stabilization of cyclic pi-systems, (ii) magnetic properties used by ring currents and (iii) structural properties were suggested [2,3,10-13].

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In the present paper, we investigate the influence of different substituents on the degree of aromaticity of benzene rings using electric field gradient. The main goal of this work is twofold: (i) the determination of aromaticity for some benzene derivatives; (ii) comparing effects of different substituents on benzene ring.

2. Computational details

The energy of the mono-substituted benzene compounds have been fully optimized at equilibrium geometries by using DFT at B3LYP level of theory with 6-311++G** [12] basis set. Frequency test has been done t ensure that all the optimized geometries are in the ground state. The optimized geometries show that all rings are planar (in xy plane). The EFG calculations at the middle of bonds according to the procedure (will be mentioned in results and discussion) have been performed for optimized structures. The calculations have been carried out by Gaussian03 [13] package.

3. Results and Discussion

The electric field gradient tensor, $\mathbf{V}^{ij}$, which is defined by the second derivatives of the potential generated by electron density with respect to desired position of molecule, is a useful tool to obtain some molecular information. The electric field gradient tensor is a symmetric second rank tensor with zero off diagonal elements which can be expressed in an axis system. This axis system, which is called the principal axis of the field gradient tensor, is diagonal and as non-zero components $\partial^2 V/\partial z^2$, $\partial^2 V/\partial y^2$, $\partial^2 V/\partial x^2$ where V is the electrostatic potential. Furthermore, it can be

shown that the field gradient tensor is traceless, i.e. $\partial^2 V/\partial z^2 + \partial^2 V/\partial y^2 + \partial^2 V/\partial x^2 = 0$ [14]. Thus, the quantity of $q = \partial^2 V/\partial z^2$ is a component which can be assigned to "EFG" in this paper. The unit of computed EFG value is Volt per square meter (Vm^{-2} or $NC^{-1}m^{-1}$).

In order to distinguish aromaticity measure by EFG procedure, the results of $EFG^{(o)}$ values for C-C bond of benzene should be analyzed. The $EFG^{(o)}$ values for C-C bond in cyclohexane as a reference is obtained. The value is 2.0309 and called "sigma contribution". Then the value is obtained for C=C bond in cyclohexene as another reference at the middle of double bond. The value ($EFG^{(o)}$ = 3.5917) is called "pi contribution".

With this calculation, it is expected three of summation of sigma and pi contributions for a compound with three double bonds and three single bonds in local form. By using B3LYP method we have: $3 \times (2.0309 + 3.5917) = 16.8678$. If we calculate $EFG^{(o)}$ for each bond in benzene, we find summation of $EFG^{(o)}$ of all bonds which is 18.0575, that is less than expected value. In other words, $\Delta EFG^{(0)} = +1.1898$ that always are positive for aromatic compounds.

EFG procedure is performed for some substituted benzene derivative with respect to the related references at the middle of the bond for evaluation of aromaticity of the compounds from this point of view.

The aromaticity values of $\Delta EFG^{(0)}$ for benzene and a series of mono-substituted benzene derivatives, which are presented in Table 1 and 2 for Hartree-Fock method and density functional method respectively, are discussed in this section. It is worth noting that $\Delta EFG^{(o)}$ values show that existing substitution on benzene make a small change in aromaticity,

which causes a minorchange in the cyclic π-electron delocalization. This effect has been also observed by other indices such as NICS(0), NICS(1) [15], HOMA [16,17] and PDI [18]. The aromaticity by three procedures (NICS(0), NICS(1) and $\Delta EFG^{(o))}$) in Table 1 consistently

matches with each other in the following groups such as fluoride, chloride, bromide and cyanide are well known aselectron withdrawing groups, but we observed that groups have not the same effects in aromaticity.

Table 1. ΔEFG values for substituted benzenes by using Hartree-Fock method
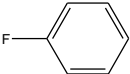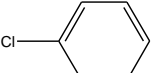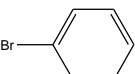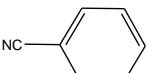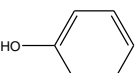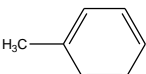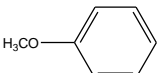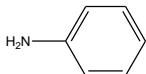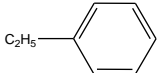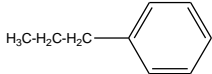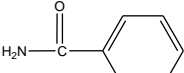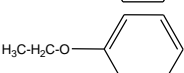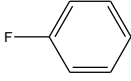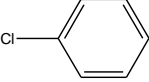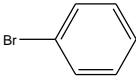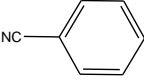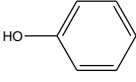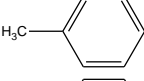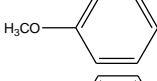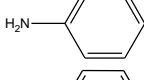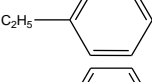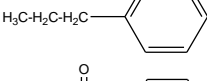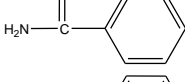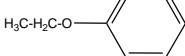
	Molecule	Scheme	M	A	B	$\Delta EFG^{(0)}$
1	Benzene		78.11	17.5347	18.7836	1.2489
2	Fluorobenzene		97.11	18.1902	19.0533	0.8631
3	Chlorobenzene		113.57	18.3264	19.0468	0.7204
4	Bromobenzene		158.02	18.1638	19.0088	0.8450
5	Cyanobenzene		104.13	17.3529	18.7869	1.4340
6	Phenol		95.12	17.877	18.8949	1.0179
7	Toluene		93.15	17.4384	18.7838	1.3454
8	Methoxybenzene		109.15	17.8554	18.9064	1.0510
9	Aniline		94.14	17.5251	18.7725	1.2474
10	Ethylbenzene		107.18	17.3949	18.7792	1.3843
11	Propylbenzene		121.20	17.40011	18.7964	1.3963
13	Benzamide		121.25	17.4567	18.8187	1.3620
14	Ethoxybenzene		123.68	17.8431	18.8976	1.0545

Table 2. Δ EFG values for substituted benzenes by using B3LYP method

	Molecule	Scheme	M	A	B	Δ EFG$^{(0)}$
1	Benzene		78.11	16.8678	18.0575	1.1898
2	Fluorobenzene		97.11	17.490	18.2834	0.7934
3	Chlorobenzene		113.57	17.3280	18.1833	0.8553
4	Bromobenzene		158.02	17.3307	18.169	0.8383
5	Cyanobenzene		104.13	16.4775	17.9934	1.5159
6	Phenol		95.12	17.0580	18.1458	1.0878
7	Toluene		93.15	16.6554	18.0089	1.3535
8	Methoxybenzene		109.15	17.0565	18.1068	1.0503
9	Aniline		94.14	16.7034	18.0373	1.3339
10	Ethylbenzene		107.18	16.6314	17.9988	1.3674
11	Propylbenzene		121.20	16.6170	17.9975	1.3805
13	Benzamide		121.25	16.7019	18.0033	1.3014
14	Ethoxybenzene		123.68	16.9905	18.089	1.0985

Also, electron donating groups have different effects on aromaticity of benzene. Therefore, the results reveal little dependency for the electron-withdrawing and electron-donating substituents.

A comparison of the values of the aromaticity index by using two methods of Hartree-Fock and density functional theory shows that the results have the same trends in predicting aromaticity through two methods.

Conclusion

Several mono-substituted derivatives of benzene have been optimized at HF/3-21G and B3LYP/6-311++G** level of theory with no imaginary frequencies. All the rings which have been optimized are planar.

Electric field gradient (EFG) calculations have been performed for these species and presented a new criterion for aromaticity, which are indicated by $\Delta EFG^{(o)}$. Positive ΔEFG values indicate the presence of aromaticity.

The EFG and energy calculation by using two methods have the same trend in conclusion. Our results have been compared with NICS(0) and NICS(1) and other well known indices in literatures and have been shown a good agreement with them. Our method is computationally much easier and inexpensive to compute. Since EFG calculations can be also obtained by some other quantum mechanical programs, this type of aromaticity evaluations can be available for most researchers.

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