

A new approach for aromaticity criterion based on electrostatic field gradient

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Abstract In this research, electric field gradient (EFG), which is the first derivative of electric field, is applied for evaluation of aromaticity of 89 cyclic organic compounds. In our calculations, DFT procedure (b3lyp) with basis set 6-311++G** has been employed, and the obtained electronic structures and frequency test has been done for optimized geometries. The aromaticity evaluated for these compounds by EFG procedure is successfully compared with other well-known indices in literature, especially with nuclear independent chemical shift (NICS). These comparisons show that EFG method of assessment of aromaticity can be used as a rather valid procedure for this purpose. Flexibility and simplicity of EFG make this method a rather easy procedure for assessment of aromaticity. Since EFG method of aromaticity evaluation does not need specific programming and it can be done by known software such as Gaussian, therefore, the availability for everyone to calculate desired aromaticity by this method is one of attractive feature of it similar to NICS.

Keywords Aromaticity · EFG · Electrostatic field gradient

Introduction

Aromaticity is the most widely used concept that plays an important role in chemistry. Conjugated planar cyclic hydrocarbon compounds, which follow $4n+2$ electrons rule, have aromaticity and also contain π -delocalization electrons. Aromatic compounds have special properties such as extra stabilization, special reactivity and magnetic properties. The concept of aromaticity has been the subject of much debate and is still attracting considerable interest. Therefore, some issues of Chemical Reviews have been dedicated to cover this topic [1–3].

Many descriptors of aromaticity have been introduced to date. Most common procedures are listed as follows: a- Clar's rule [4, 5] and chemical graph theory (CGT) index [6, 7] b- Numerical Kekule valence structure “(NKVS) [8, 9] c- Aromatic stabilization energy (ASE) substituted effect stabilization energy (SESE) and out-of-plane ring deformation energy (E_{def}) [10] d- Harmonic oscillator model of aromaticity (HOMA) based on geometry [11] e- Multicenter bond indices or n-center delocalized indices (n-DI's) [12–16] introduced and propagated by Mosquera and Sola and others [17–24] f- Para delocalization index (PDI), [25] g- Aromatic fluctuation index (FLU) [26] h- The average two-center indices (ATI) [27] i- I_{NG} and I_{NB} indices based on the Hückel molecular orbital (HMO) approximation [28–30] j- Electrophilic aromatic substitution (EAS) k- H-NMR chemical shift Nucleus-independent chemical shift (NICS). [31–33]

In this research, a new procedure for evaluation of aromaticity of cyclic compounds is presented. EFG has been used before in literature to evaluate nuclear quadrupole resonance (NQR) in various properties of molecules [34–38]. Nonetheless it is the first time, EFG is being used for aromaticity evaluation.

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Computational details

All the compounds have been fully optimized energies at equilibrium geometries by using DFT at B3LYP level with 6-311++G** [39] basis set. Frequency test has been done to ensure that all the optimized geometries are in ground state. The optimized geometries show that all rings are planar (in xy plane). The EFG calculations at the sites of atoms and in the middle and above the bonds have been made according to the procedure (see Results and discussion below) for optimized structures. The calculations have been done by Gaussian03 [40] package.

Results and discussion

The electric field gradient tensor, 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 with 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., $\partial^2 V / \partial z^2 + \partial^2 V / \partial y^2 + \partial^2 V / \partial x^2 = 0$ [41]. 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 $\text{NC}^{-1} \text{m}^{-1}$). The keyword of prop=EFG, should be used in Gaussian03 for evaluation of EFG.

The EFG value can be measured at various points of the molecule, e.g., on the atom and any points on/out of bond. EFG values at zero point on atom or any other points on A-B bond distance, presented by $\text{EFG}^{(0)}$, means that EFG value is evaluated for the same Cartesian coordinates as for the atom or any point at inter-atomic bond distance. In

order to demonstrate the changes in the EFG values at different positions of the molecule, $\text{EFG}^{(0)}$ values are calculated on the atom or any points of the bond distance. Then, the distance from 0.0 to 2.0 Å (0.1 Å in each step) on the perpendicular line to the molecular plane is gradually increased, and EFG is calculated at each point, as shown in Fig. 1 for the benzene ring as an example. The above procedure has been followed for ethane, ethylene, acetylene and benzene, presented in Table 1. These results show that $\text{EFG}^{(0)}$ value on the atom is minimum, it rapidly goes to the maximum at 0.1 Å, and then, EFG values gradually decline and vanish at the point of 2.0 Å. Nevertheless, EFG value in the middle of the bond distance has the maximum value. This maximum value decreases gradually and vanishes at the point of 2.0 Å. Since EFG value of each point of the bond distance and the perpendicular line to the bond distance do not show any particular preference, EFG values for the two arbitrary points of the middle of bond distance, at the zero point ($\text{EFG}^{(0)}$) and at 0.5 Å above the bond ($\text{EFG}^{(0.5)}$), have been chosen for all molecular systems throughout this article. This is similar to the points of 0.0 and 1.0 in NICS index by Schleyer [31].

In order to distinguish bond order of single, double and triple bonds by EFG procedure, the results of $\text{EFG}^{(0)}$ and $\text{EFG}^{(0.5)}$ values for C-C bond of some molecules such as ethane, ethylene and acetylene in Table 1 should be analyzed. The $\text{EFG}^{(0)}$ values for C-C bond in ethane, ethylene and acetylene have been obtained 2.0548, 3.6325 and 5.1470, respectively. The $\text{EFG}^{(0)}$ value difference between ethylene and ethane for C-C bond distance is 1.5777, which can be attributed to “*ethylenic π -bond*”. Similarly, the difference between $\text{EFG}^{(0)}$ values of acetylene and ethane is about 3.0922 which is attributed to “*acetylenic π -bond*”. Interestingly, $\text{EFG}^{(0)}$ for acetylenic was about twice as much for ethylenic as expected. The $\text{EFG}^{(0.5)}$ values exhibit the same trend as $\text{EFG}^{(0)}$. The $\text{EFG}^{(0.5)}$ values for ethane, ethylene and acetylene were 0.9140, 1.3874 and 1.8810, respectively. If the $\text{EFG}^{(0.5)}$

Fig. 1 The selected points for computing EFG values; a- at the middle and above bond distance. b- on atom and above

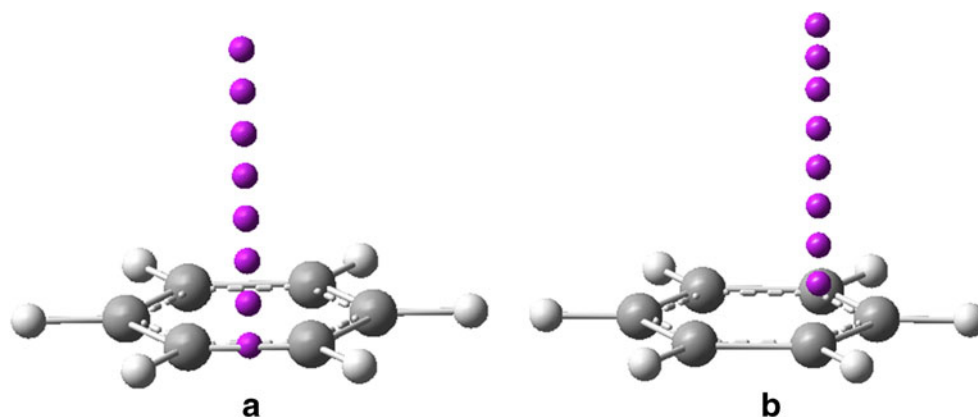


Table 1 Electric field gradient of ethane, ethylene, acetylene and benzene (in volt per square meter) at different distances on atom and bond (in angstroms)

Distance	Electric field gradient							
	Ethane		Ethylene		Acetylene		Benzene	
	^a On C-C bond	On C atom	On C-C bond	On C atom	On C-C bond	On C atom	On C-C bond	On C atom
0	2.0548	0.0279	3.6325	0.2373	5.1470	0.3123	3.0064	0.1866
0.1	1.9810	836.9538	3.2992	836.6125	4.8985	838.1547	2.7671	836.9540
0.2	1.7797	88.1855	2.9176	88.1733	4.2574	88.3729	2.4597	88.1727
0.3	1.4998	23.4214	2.4033	23.4107	3.4257	23.4904	2.0316	23.3988
0.4	1.1969	9.4786	1.8679	9.4433	2.5950	9.4873	1.6002	9.4326
0.5	0.9140	4.7328	1.3874	4.6614	1.8810	4.6839	1.1986	4.6521
0.6	0.6743	2.6517	0.9959	2.5465	1.3195	2.5551	0.8672	2.5380
0.7	0.4847	1.6002	0.6968	1.4705	0.9060	1.4706	0.6110	1.4690
0.8	0.3418	1.0208	0.4779	0.8793	0.6064	0.8749	0.4218	0.8784
0.9	0.2377	0.8323	0.3226	0.5390	0.4094	0.5327	0.2865	0.5376
1.0	0.1640	0.6782	0.2149	0.3366	0.2714	0.3297	0.1923	0.3310
1.5	0.0286	0.0687	0.0245	0.0378	0.0334	0.0359	0.0238	0.0363
2.0	0.0063	0.0102	0.0016	0.0064	0.0034	0.0026	0.0027	0.0043

^a refers to middle of Carbon-Carbon bond

values difference between ethylene and ethane, the $EFG^{(0.5)}$ contribution of ethylenic π -bond would be 0.4734. The corresponding value between acetylene and ethane were measured. The $EFG^{(0.5)}$ value for acetylenic would be 0.9670. Thus, the latter value is about twice that of the former.

How to calculate the aromaticity of benzene from EFG point of view? EFG procedure for evaluation of aromaticity is as follows. Let us use $EFG^{(0.5)}$ for this analysis without losing the generality of the concept. It is observed that $EFG^{(0.5)}$ values of six C-C bonds are all equal, and that is 1.1986 which is between the single bond of ethane and the double bond of ethylene ($0.9140 < 1.1986 < 1.3874$). This clearly confirms the existence of “delocalization” of π bonds in this molecule. EFG value for benzene as a localized form is three times ethylenic bonds, (3×0.4734) = 1.4202. If benzene is considered as a delocalized form, then π -delocalization contribution of EFG in benzene would be;

$$\begin{aligned} & \sum EFG^{(0.5)} \\ &= \left(6 \times EFG^{(0.5)} \right)_{\text{of benzene}} - \left(6 \times EFG^{(0.5)} \right)_{\text{of ethane}} \\ &= (6 \times 1.1986) - (6 \times 0.9140) = 1.7076. \end{aligned}$$

Thus, the aromaticity of $\Delta EFG^{(0.5)}$ for benzene would be;

$$\Delta EFG^{(0.5)} = 1.7076 - (3 \times 0.4743)_{\text{of ethylenic}} = 0.2874,$$

which has been shown in Tables 2, 3, 4, and 5. The aromaticity of many compounds has been evaluated by the mentioned procedure in eight tables. These tables clearly reveal that $\Delta EFG^{(0.5)}$ value is positive for all aromatic systems. It is worth noting that H_2N-NH_2 and $HN=NH$ or H_2N-CH_3 and $HN=CH_2$ should be considered for their contribution of single and localized double bonds for heterocyclic compounds.

In order to show EFG procedure for antiaromaticity, some known antiaromatic compounds have been chosen to test. First, the aromaticity of cyclobutadiene has been evaluated by the same procedure as for benzene. The results show that there are two single bonds with $EFG^{(0.5)}$ of 0.8262 and two double bonds with $EFG^{(0.5)}$ of 1.3446. Therefore,










$$\begin{aligned} \sum EFG^{(0.5)} &= 2(1.3446 + 0.8262)_{\text{of cyclobutadiene}} \\ &\quad - (4 \times 0.9140)_{\text{of ethane}} = 0.6856. \end{aligned}$$

The $EFG^{(0.5)}$ value for cyclobutadiene as a localized form is twice of ethylenic (2×0.4734)_{of ethylenic}. Accordingly, the aromaticity of $\Delta EFG^{(0.5)}$ for cyclobutadiene would be,

$$\Delta EFG^{(0.5)} = 0.6856 - (2 \times 0.4735)_{\text{of ethylenic}} = -0.2613.$$

Therefore, $\Delta EFG^{(0.5)}$ value is negative for antiaromatic compounds. Several known antiaromatic compounds have been tested and the results are: for cyclopropene anion (-0.2344), cyclopentadiene cation (-0.1440), benzene dication (-0.1184), alumol (-0.0068), borol (-0.0560), benzocyclobu-

Table 2 NICS and Δ EFG values for substituted benzenes














Molecule		NICS(0)	NICS(1)	Δ EFG ⁽⁰⁾	Δ EFG ^(0.5)
Benzene		-8.03	-10.20	0.9768	0.2874
Benzene-F		-9.98	-10.39	1.2120	0.2912
Benzene-Cl		-8.81	-10.05	1.1212	0.2870
Benzene-Br		-8.52	-9.88	1.0887	0.1592
Benzene-NO ₂		-9.97	-10.47	1.5891	0.4990
Benzene-CHO		-7.68	-10.11	0.9016	0.2755
Benzene-COOH		-7.95	-10.15	0.9383	0.2864
Benzene-OH		-9.06	-9.82	1.0829	0.2547
Benzene-CN		-9.44	-10.23	0.9327	0.2596

tadiene (-0.3466) and biphenylene (-0.4998). These results reveal that *negative* value of Δ EFG is an indication of antiaromaticity.

Aromaticity is a property with a theoretical definition and cannot be measured experimentally. Therefore, it is not easy to identify correct indices among the several reported

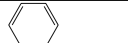
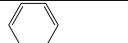

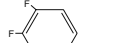
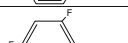
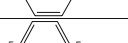
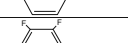
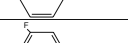
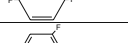
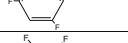
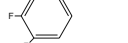
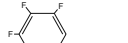
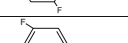
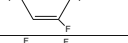
indices. Schleyer [31] in 2005 identified and explained certain problems with some indices. The results obtained by our EFG procedure have been compared with Schleyer's results, nuclear independent chemical shift (NICS(0) and NICS(1) in ppm unit [31]) which are reported in tables, because the Schleyer's results contain a variety of aromatic

Table 3 NICS and Δ EFG values for hydroxy benzenes

Molecule		NICS(0)	Mean*	NICS(1)	Mean	Δ EFG ⁽⁰⁾	Mean	Δ EFG ^(0.5)	Mean
Benzene		-8.03		-10.20		0.9768		0.2874	
Hydroxybenzene		-9.06		-9.82		1.0829		0.2547	
1,2-Dihydroxybenzene		-10.39	-10.06	-9.97	-9.62	1.1830	1.1811	0.2178	0.2197
1,3-Dihydroxybenzene		-9.73		-9.26		1.1678		0.2157	
1,4-Dihydroxybenzene		-10.19		-9.63		1.1924		0.2257	
1,2,3-Trihydroxybenzene		-11.49	-11.01	-9.88	-9.27	1.2276	1.2405	0.1786	0.1726
1,2,4-Trihydroxybenzene		-11.34		-9.58		1.2353		0.1661	
1,3,5-Trihydroxybenzene		-10.20		-8.36		1.2586		0.1731	
1,2,3,4-Tetrahydroxybenzene		-12.98	-12.58	-10.11	-9.71	1.3293	1.3701	0.1278	0.1397
1,2,3,5-Tetrahydroxybenzene		-12.12		-9.25		1.3780		0.1423	
1,2,4,5-Tetrahydroxybenzene		-12.63		-9.76		1.4031		0.1490	
1,2,3,4,5-Pentahydroxybenzene		-14.03		-10.10		1.4448		0.1111	
Hexahydroxybenzene		-15.52		-10.70		1.4923		0.0597	

* mean is absolute mean value from now on in this article

Table 4 NICS and ΔEFG values for fluorinated benzenes

Molecule		NICS(0)	Mean	NICS(1)		$\Delta EFG^{(0)}$	Mean	$\Delta EFG^{(0.5)}$	Mean
Benzene		-8.03		-10.20		0.9768		0.2874	
Fluorobenzene		-9.98		-10.39		1.2120		0.2903	
1,2-Difluorobenzene		-11.76	-11.39	-10.67	-10.50	1.3740	1.3636	0.2666	0.2804
1,3-Difluorobenzene		-11.70		-10.40		1.4402		0.2852	
1,4-Difluorobenzene		-11.60		-10.43		1.2767		0.2894	
1,2,3-Trifluorobenzene		-13.39	-13.33	-10.85	-10.60	1.5036	1.5805	0.2301	0.2536
1,2,4-Trifluorobenzene		-13.43		-10.69		1.5904		0.2585	
1,3,5-Trifluorobenzene		-13.16		-10.25		1.6476		0.2723	
1,2,3,4-Tetrafluorobenzene		-15.19	-15.12	-11.17	-10.99	1.6462	1.6924	0.1979	0.2135
1,2,3,5-Tetrafluorobenzene		-14.94		-10.79		1.7072		0.2172	
1,2,4,5-Tetrafluorobenzene		-15.22		-11.01		1.7237		0.2254	
1,2,3,4,5-Pentafluorobenzene		-16.74		-11.40		1.7563		0.1559	
Hexafluorobenzene		-18.23		-11.93		1.7921		0.1443	

systems to compare with. Although the NICS(0) π_{zz} is the best index among NICS indices for planar π molecule, we would rather the above indices, i.e., NICS(0) and NICS(1) in order to compare the aromaticity of compounds [42].

We would like to express our view before presenting our method and discussion. Since there are no experimental values for aromaticity, it is not possible to claim which index gives you more accurate results. Therefore, we are only interested in presenting our new approach.

Substituted benzenes

The aromaticity values of $\Delta EFG^{(0.5)}$ for benzene and a series of monosubstituted benzene derivatives, which are presented in Table 2, are discussed in this section. It is worth noting that both $\Delta EFG^{(0.5)}$ and $\Delta EFG^{(0)}$ values show that the existing substitution on benzene makes a small change in aromaticity, which causes a minor change in the cyclic π -electron delocalization. This effect has also been observed in other indices such as NICS(0), NICS(1) [43], HOMA [44, 45] and PDI [46]. The aromaticity by four procedures (NICS(0), NICS(1), $\Delta EFG^{(0)}$ and $\Delta EFG^{(0.5)}$) in Table 2 consistently matches with one another in the following cases, fluorobenzene and nitrobenzene have

higher aromaticity than benzene, while benzene with substituents CHO and COOH have less aromaticity than benzene, and with substituents Cl, Br and OH have more aromaticity than benzene by NICS(0) and $\Delta EFG^{(0)}$, but they have less aromaticity than benzene by NICS(1) and $\Delta EFG^{(0.5)}$. Cyanobenzene has more aromaticity than benzene by both procedures of NICS, while by both procedures of EFG values show the reverse results. These exceptions (fluorobenzene and nitrobenzene) have been reported by SESE and ASE values [43, 44]. The study of substituted benzene derivatives also reveals that aromaticity of fluorobenzene is more than aromaticity of phenol which is accords with the results by NICS(0), NICS(1) [31], PDI [47], E_{def} [10], ASE and ESES methods [48].

It would be interesting to discuss multi-substituted hydroxybenzene. Let us define the *mean value* as an average of aromaticity for all possible isomers. From now on, absolute mean value of aromaticity for multi-substituted isomers will be considered in our discussion, unless stated otherwise. The results presented in Table 3 for the multi-hydroxybenzene compounds show that greater number of hydroxy groups substituted in benzene ring cause greater mean values of aromaticity in comparison with benzene by NICS(0), NICS(1) and $\Delta EFG^{(0)}$, while all mean values by

Table 5 NICS and Δ EFG values for various selected substituted benzenes


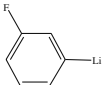
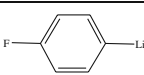
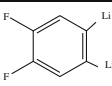
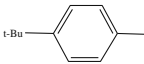
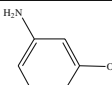
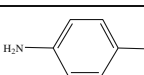
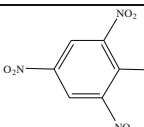
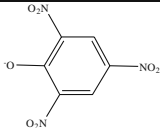
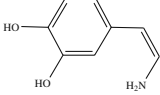
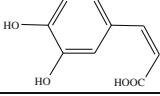
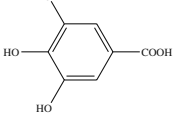
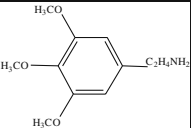
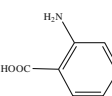
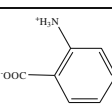
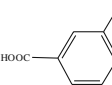
No.	Molecule		NICS(0)	NICS(1)	Δ EFG ⁽⁰⁾	Δ EFG ^(0.5)
	Benzene		-8.03	-10.2	0.9768	0.2874
1	(3-Fluorophenyl)lithium		-8.82	-10.10	0.8391	0.2429
2	(4-Fluorophenyl)lithium		-9.13	-10.23	0.8261	0.2387
3	1,2-Difluoro-4,5-dilithiobenzene		-9.82	-10.14	0.5858	0.1535
4	4-tert-Butiphenol		-9.18	-9.81	1.0317	0.2337
5	3-Aminophenol		-8.05	-8.52	1.0411	0.2116
6	4-Aminophenol		-9.23	-9.05	1.1095	0.2122
7	2,4,6-Trinitrophenol		-11.04	-9.30	0.9862	0.1469
8	2,4,6-Trinitrophenolate		-5.34	-5.20	0.1731	0.0149
9	4-(2-Aminopropyl)benzene-1,2-diol		-10.24	-9.71	1.0925	0.1950
10	(2Z)-3-(3,4-Dihydroxyphenyl)acrylic acid		-9.75	-13.1	1.1720	0.2018
11	3,4,5-Trihydroxybenzoic acid		-11.50	-10.02	1.2215	0.1624
12	3,4,5-Trimethoxyphenylamine		-11.18	-9.78	1.0329	0.1561
13	2-Aminobenzoic acid		-6.75	-8.11	1.1525	0.1591
14	2-Aminobenzoic acid (zwitter ionic)		-7.87	-8.98	0.9361	0.2611
15	3-Aminobenzoic acid		-7.87	-8.98	0.9270	0.2187

Table 5 (continued)

16	3-Aminobenzoic acid (zwitter ionic)		-9.71	-10.55	1.1525	0.2136
17	4-Aminobenzoic acid		-7.34	-8.80	0.8921	0.2098
18	4-Aminobenzoic acid (zwitter ionic)		-9.31	-10.33	1.1078	0.2967
19	4-(Dimethylamino) benzonitrile		-7.94	-9.02	0.7678	0.1820
20	2-Aminobenzenaminium		-9.25	-10.20	1.1728	0.2469

$\Delta\text{EFG}^{(0.5)}$ have reverse trend (the mean value of trihydroxybenzene isomers is an exception by NICS(1)).

The result of the analysis of multi-fluorobenzene results in Table 4 show that the results by four procedures (NICS(0), NICS(1), $\Delta\text{EFG}^{(0)}$ and $\Delta\text{EFG}^{(0.5)}$) consistently match with each other in such a way that the mean values of the first three procedures have more fluoro group and more aromaticity, while the last one ($\Delta\text{EFG}^{(0.5)}$) has reverse trend in aromaticity. Maksic [49] has reached similar conclusions for multi-fluorobenzenes by setting some theoretical reactions, however, ab initio block-localized wavefunction computations reveal that perfluorobenzene C_6F_6 is as aromatic as benzene [50]. It is interesting to note that para-difluorobenzene has stronger aromaticity than para-dihydroxybenzene, which is confirmed [47] by HOMA, NICS(1)_{ZZ} and ASE indices.

It is also interesting to compare multi-hydroxybenzene and multi-fluorobenzene trend in Tables 3 and 4, which show that the trend of NICS(0), NICS(1), $\Delta\text{EFG}^{(0)}$ and $\Delta\text{EFG}^{(0.5)}$ in both categories of compounds are the same, with only one exception for trihydroxybenzene isomers.

It seems that the symmetry of the molecule is a factor that can increase the aromaticity of benzene derivatives within different isomers by both of the EFG procedures. The symmetric substituted benzene for multi-hydroxyl or multi-fluoro benzene (for di, tri and tetra substitutions) which has the highest aromaticity have been compared with the other isomers perhaps by push-pull mechanism. For instance, 1,4-difluorobenzene and 1,4-dihydroxybenzene with more symmetry are more aromatic than other disubstituted isomers among similar ones, as shown in Tables 3 and 4 (with the exception of 1,4-difluorobenzene by $\Delta\text{EFG}^{(0)}$). Krygowski et al. [47] have reported that para-difluorobenzene by NICS(1)_{ZZ} SESE indices and para-dihydroxybenzene by using SESE, NICS(0), NICS(1) and NICS(1)_{ZZ} indices show more aromaticity than meta

isomers. This trend for NICS(0) and NICS(1) in Tables 3 and 4 is considered with only a few exceptions.














In order to test the aromaticity of the substituted benzene with a variety multisubstitution by EFG procedure, 20 molecules have been chosen with different substituents, the results of which are presented the results in Table 5. The results show that for different multi-substituents for NICS(0) and $\Delta\text{EFG}^{(0)}$, the aromaticity are more than benzene, except for compounds No. 8, 14, 15, 17 and 19 for the procedures, and for $\Delta\text{EFG}^{(0)}$ only No. 1, 2 and 3. But for NICS(1) and $\Delta\text{EFG}^{(0.5)}$, the aromaticity is less than for benzene, except for compounds No. 2, 10, 16 and 18 for NICS. It is interesting that 2,4,6-trinitrophenolate compound (No. 8) has the minimum aromaticity consistently by four procedures.

Heterocyclic compounds

The aromaticity of hetero-monocyclic compounds containing nitrogen such as azapyridines and azapyrroles has been computed by EFG method. The results of azapyridines, which is presented in Table 6, display a decrease of the aromaticity with the number of nitrogens, if aromaticity is measured by NICS(0) and $\Delta\text{EFG}^{(0)}$. There is one exception for pentaazapyridine, which has more aromaticity than pyridine for $\Delta\text{EFG}^{(0)}$, while NICS(0) cannot predict aromaticity for this compound. The mean values of aromaticity evaluated by NICS(1) and $\Delta\text{EFG}^{(0.5)}$ for azapyridine compounds increases as the number of nitrogens increase in such a way that pentaazapyridine has maximum aromaticity. Besides, the study on pyridines done by Giambiagi et al. [51] by using data of I_{ring} and RCI (ring current index) [52, 53] confirms the obtained EFG^(0.5) trend in di, tri, tetra and pentaazapyridines.

The mean values of aromaticity for azapyrrole compounds measured by all four procedures; i.e., NICS(0), NICS(1), $\Delta\text{EFG}^{(0)}$ and $\Delta\text{EFG}^{(0.5)}$, presented in Table 7,

Table 6 NICS and Δ EFG values for aza pyridines

Molecule		NICS(0)	Mean	NICS(1)	Mean	Δ EFG ⁽⁰⁾	Mean	Δ EFG ^(0.5)	Mean
Pyridine		-6.82		-10.17		0.8876		0.3515	
2-Azapyridine		-5.33	-5.38	-10.53	-10.25	0.7342	0.7737	0.4146	0.3930
3-Azapyridine		-5.51		-9.99		0.8063		0.3860	
4-Azapyridine		-5.30		-10.24		0.7805		0.3704	
2,3-Diazpyridine		-4.32	-4.04	-10.80	-10.27	0.8658	0.7422	0.5298	0.4611
2,4-Diazpyridine		-3.77		-10.36		0.6364		0.4356	
3,5-Diazpyridine		-4.04		-9.65		0.7244		0.4179	
2,3,4-Triazapyridine		-2.67	-2.28	-10.78	-10.57	0.7068	0.7474	0.5902	0.5506
2,3,5-Triazapyridine		-2.37		-10.36		0.7779		0.5465	
2,4,5-Triazapyridine		-1.80		-10.58		0.7576		0.5152	
2,3,4,5-Tetraazapyridine		-0.62		-10.64		0.8505		0.6844	
Pentaazapyridine		+1.86		-10.24		0.9566		0.8371	

consistently show an increase as the number of nitrogens increases, except for diazapyrrole isomers of Δ EFG⁽⁰⁾. Mandado et al. [54] have shown the same trend as EFG^(0.5) through studying on azapyrroles by using n-center delocalization index.

A further trend is that the isomers with adjacent nitrogens in the ring usually have more aromaticity than

other isomers with nonadjacent nitrogens (or sometimes with little descreitency), such as 2-, 2,3-, 2,3,4- and 2,3,4,5-azapyridine in Table 6, or 2-, 2,3- 2,3,4- 2,3,5- azapyrrole in Table 7. Therefore, pentaazapyridine and tetraazapyrrole are expected to be the most aromatic compounds in their categories by the trend, and the results confirm this expectation by four procedures. These results are in

Table 7 NICS and Δ EFG values for aza pyrroles






















Molecule		NICS(0)	Mean	NICS(1)	Mean	Δ EFG ⁽⁰⁾	Mean	Δ EFG ^(0.5)	Mean
Pyrrole		-13.62		-10.09		1.4484		0.2261	
2-Azapyrrole		-13.61	-13.35	-11.30	-10.92	1.7877	1.7777	0.3530	0.3290
3-Azapyrrole		-13.10		-10.55		1.7677		0.3054	
2,3-Diazapyrrole		-13.97	-13.66	-12.73	-12.08	1.7270	1.5004	0.4338	0.3961
2,4-Diazapyrrole		-13.09		-11.57		1.4197		0.3511	
2,5-Diazapyrrole		-13.64		-11.28		1.6160		0.4984	
3,4-Diazapyrrole		-13.95		-12.76		1.2390		0.3012	
2,3,4-Triazapyrrole		-14.33	-14.40	-13.49	-13.64	1.9634	2.0182	0.5292	0.5440
2,3,5-Triazapyrrole		-14.46		-13.89		2.0730		0.5589	
2,3,4,5-Tetraazapyrrole		-16.72	-	-15.76		2.4688		0.7663	

Table 8 NICS and Δ EFG values for phosphapyrroles

Molecule		NICS(0)	Mean	NICS(1)	Mean	Δ EFG ⁽⁰⁾	Mean	Δ EFG ^(0.5)	Mean
Pyrrole		-13.62		-10.09		1.4485		0.2261	
2-Phosphapyrrole		-12.96	-13.20	-10.47	-10.66	1.2165	1.2944	0.1469	0.1718
3-Phosphapyrrole		-13.45		-10.86		1.3724		0.1968	
2,3-Diphosphapyrrole		-13.55	-12.88	-11.28	-11.04	0.9289	1.0893	0.1708	0.1151
2,4-Diphosphapyrrole		-12.85		-11.19		1.0452		0.0875	
2,5-Diphosphapyrrole		-11.95		-10.78		0.9257		0.0459	
3,4-Diphosphapyrrole		-13.18		-10.90		1.4575		0.1561	
2,3,4-Triphosphapyrrole		-14.44	-13.68	-12.24	-12.00	0.9929	0.7928	0.1168	0.0866
2,3,5-Triphosphapyrrole		-12.93		-11.77		0.5928		0.0565	
2,3,4,5-Tetraphosphapyrrole		-15.46		-13.42		0.5144		0.0787	

agreement with n-center delocalization index presented by Mandado et al. [54] in 2006. Cioslowski's report in 2007 [30] also gives us the same trend of aromaticity for some heterocyclic compounds such as pyridazine (2-azapyridine), pyridine and pyrazine (4-azapyridine).








Another heterocyclic class consists of the compounds with two heteroatoms, nitrogen and phosphorus. The results in Table 8 show that the existence of two heteroatoms perturbs more π -electron delocalization, consequently, they have less aromaticity in comparison with azapyrroles.

Three trends have been found in EFG results in Table 8. The first trend states that the aromaticity increase with the

number of phosphorus atoms in phosphapyrrole rings increases the aromaticity when Δ EFG⁽⁰⁾ and NICS(0) are applied, while this trend is reverse for applying Δ EFG^(0.5) and NICS(1).

The second trend states that increasing the number of P-P bonds increases the aromaticity of the molecules within specific isomers especially when it has H-N-P-P structure. For instance, within four isomers of diphosphapyrroles, 2,3-diphosphapyrrole and 3,4-diphosphapyrrole have more aromaticity, and the aromaticity of 2,3-diphosphapyrrole is more than 3,4-diphosphapyrrole, because P-P is next to NH. This trend can also be seen in azapyrroles for

Table 9 NICS and EFG value for selected systems with two, three and four fused rings

Molecule		NICS(0)	NICS(0)	NICS(1)	NICS(1)	Δ EFG ⁽⁰⁾	Δ EFG ⁽⁰⁾	Δ EFG ^(0.5)	Δ EFG ^(0.5)
		A	B	A	B	A	B	A	B
Naphthalene		-8.55	-	-10.71	-	0.4666	-	0.1461	-
Anthracene		-7.50	-11.47	-9.80	-13.06	0.2803	0.1061	0.0384	0.0202
Phenanthrene		-8.53	-5.72	-10.71	-8.40	0.4712	0.1669	0.3303	0.2474
Biphenylene		-2.45	+19.25	-4.76	+9.50	+0.8913	-1.4787	+0.0850	-0.4998
Benzocyclobutadiene		-0.50	+23.67	-2.80	13.66	+0.5857	-0.9345	+0.4529	-0.3466
Pyrene		-11.27	-13.03	-3.88	-6.62	0.3930	0.0661	0.1996	0.0994
Coronene		-9.46	+0.39	-11.59	-4.07	0.1016	-0.5375	0.1010	-0.1081

compounds containing NH-N-N in Table 7. Therefore, this may be generalized when heteroatom-heteroatom bond is next to NH, which causes more aromaticity.

The third trend is that azapyrroles compounds have more aromaticity than the corresponding phosphapyrroles. If there is one kind of heteroatom, the ring current is well established due to the similarity of p orbitals. This means that two 2p orbitals involved in making π -system in azapyrroles can overlap better than 2p and 3p in phosphapyrroles. For example, for $\Delta\text{EFG}^{(0.5)}$, 3-azapyrrole (0.3054) has more aromaticity than 3-phosphapyrrole (0.1968).

Polycyclic compounds

Aromaticity of compounds with more than one cyclic ring has been computed and is reported in Table 9. In naphthalene, the aromaticity of each ring is not more than benzene. HOMA [55], PDI [55], FLU [55], ATI [58], SCI [56], I_{NG} [30], I_{NB} [30] and I_{ring} [52] also confirm our results. For anthracene, ring A is more aromatic than ring B, which is confirmed by I_{NG} [30], I_{NB} [30], RC [52], FLU [55], SCI [56], n-DI [57, 58] and ATI [58] procedures and is in contrast to NICS values. In phenanthrene, the outer ring is more aromatic than the inner ring which is similar to the trend of NICS [31, 55], I_{NG} [30], I_{NB} [30], I_{ring} [52], SCI [56], HOMA [55], RC [52], PDI [55], ATI [58] and n-DI [58]. For biphenylene and benzocyclobutadiene rings, ring A is aromatic, while ring B does not show any aromaticity. This is confirmed by NICS values [31], HOMA [55] and I_{ring} [52] indices. The calculation of both EFG procedures for pyrene shows that ring A is more aromatic than ring B. I_{ring} [52] data and both NICS indices confirm our results. EFG calculation for coronene shows that ring A has aromaticity, while ring B does not, as reported through NICS and I_{ring} [52]. Buhl [59] and Moran et al. [60] evaluated the NICS values for coronene and noted that ring A was diatropic with large negative NICS values whereas ring B has a much smaller positive or negative NICS values [61] that clearly confirms our results.

A comparison between our results and NICS presented in Table 9, yields for phenanthrene, biphenylene, benzocyclobutadiene, and coronene, a consistent correlation between the EFG and the NICS method which were both applied at two places.

It is well-recognized that Diels-Alder (DA) reaction takes place via a mechanism through an aromatic transition state (TS) [62]. Some powerful methods such as NICS and PDI indices can exhibit this property, while other methods such as FLU and HOMA indices fail to account for the aromaticity of the TS. The aromaticity of the TS of Diels-Alder reaction between ethene and 1,3-butadiene to yield cyclohexene was analyzed. The results revealed the positive value of $\text{EFG}^{(0.5)}$ ($\text{EFG}^{(0.5)}=0.4307$) for the TS. It is

notable that this method is successful to detect the aromaticity of this TS, similar to NICS and PDI indices.

The source of error in EFG procedure for aromaticity calculation is that bond length of localized C-C π -bond in ethylene is assumed to be equal to the corresponding delocalized one in aromatic compounds such as benzene. Therefore, the contribution EFG of σ -bond of aromatic compounds such as benzene is actually assumed to be equal to EFG of σ -bond of ethane. This error is inevitable in all calculations, but it is not very significant. However, very small ΔEFG results, which lie in borderline of aromatic and antiaromatic, cannot be fully trusted.

Conclusions

Several series of various cyclic compounds have been optimized at 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 $\Delta\text{EFG}^{(0)}$ and $\Delta\text{EFG}^{(0.5)}$. Positive ΔEFG values indicate the presence of aromaticity, whereas negative values denote antiaromaticity.

The EFG method has been employed to study the aromaticity of 89 cyclic compounds such as substituted benzenes, heterocyclic and polycyclic compounds. Our results have been compared to those of NICS(0) and NICS(1) and other well-known indices in literature and have shown rather good agreement with them. Our method is computationally much easier and inexpensive to compute. Since EFG calculations are used the most in some other quantum mechanical programs, this type of aromaticity evaluations will be readily available.

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