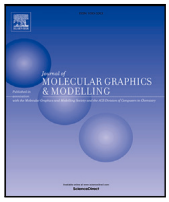
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Aromaticity of six-membered nitro energetic compounds through molecular electrostatic potential, magnetic, electronic delocalization and reactivity-based indices

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ABSTRACT

The electron density depletion associated with π-hole at the ring center typical of energetic compounds was clearly revealed by the molecular electrostatic potential (ESP). In addition, the spatial arrangement of NO_2 groups appears to affect the ESP value in the ring center, and therefore sensitivity to detonation. Indeed, for monocyclic nitrobenzene compounds with the same number of NO_2 groups, the ESP value in the ring center decreases as the NO_2 groups are more closely spaced. As expected, the central rings become less aromatic as NO_2 groups are added. The MCI, PDI, PLR, $NICS_{zz}(1)$, FLU indices are all strongly correlated with the ESP values observed in the ring center of the set of nitrobenzenes. Aromaticity indices based on electron delocalization criteria appear to be very sensitive to small variations in aromaticity. Among magnetic-based indices, only $NICS_{zz}(1)$ is capable to predict small changes in aromaticity. The PLR index derived from conceptual DFT is quite relevant for predicting small variations in aromaticity. According to our results, the most suitable aromaticity index is not based on a single criterion, and that selecting it is more subtle. Therefore, it is important to combine information from several criteria to obtain a more complete description of the aromaticity of the studied compounds.

1. Introduction

Nitroaromatic compounds are largely derived from human activities and are rarely found in nature. These compounds are widely used in manufacturing, particularly in the synthesis of dyes, polymers, pesticides and explosives [1–4]. The reactivity of these compounds is mainly governed by the electron-withdrawing nature of the nitro groups. The high electronegativity of the nitro group arises through the simultaneous action of the two electron-deficient oxygen atoms bonded to the partially positive nitrogen atom. When such a substituent is attached to a benzene ring, the NO_2 group tends to delocalize the ring's π-electrons to overcome its intrinsic charge deficiency. The delocalization of π electrons directly affects many aspects of the properties of these compounds, such as thermodynamic stability, and reactive sites.

Conjugated cyclic compounds show high diamagnetic susceptibility, and this magnetic irregularity is associated with the ring current [5]. The difficulty lies in quantifying the π-electron delocalization that causes this ring current [6]. Since Hückel's rules of thumb on aromaticity describing the electronic cyclic delocalization, it is definitely accepted that the aromatic character of a molecule implies a higher stability compared to molecules with similar structures but not aromatic [7–9]. Pauling and Sherman were the first to describe aromaticity in quantitative terms, through the concept of resonance energy [10]. Although aromaticity is a fundamental concept in modern chemistry, its exact definition is still not established [11]. As aromaticity is not a measurable magnitude, it is commonly assessed indirectly by quantifing a property which reveals the aromatic nature of the whole or portions of a molecule. However, it is commonly accepted that aromaticity is akin to electronic delocalization in conjugated chemical bonds that form closed loops, either in two or three dimensions [12,13]. The idea behind this concept is that aromaticity is proportional to the ring current strength induced by the π-electrons delocalization. Certainly, the concept of aromaticity plays a major role in rationalizing reactivity of aromatic compounds, and represents a stabilizing factor [14]. Recently, several descriptors based on energetic, magnetic, structural and chemical reactivity criteria have been proposed to quantify aromatic

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character [15–20]. Conceptually, magnetic properties are more tightly linked to aromaticity, as they depend primarily on induced cyclic currents related to the electron delocalization. From this point of view, NICS (Nucleus-Independent Chemical Shift) [21] emerges as the most popular method for assessing aromaticity in terms of magnetic criteria [12]. The correlation between shielding and ring current strength has already been quantitatively investigated, and spatial dependencies between the two magnitudes have been established [22,23].

The NICS-based indices evaluate the extent of aromaticity according to the magnetic criteria, which measures paratropicity/diatropicity of the created ring current through the effective magnetic shielding. These indices are based on the NMR chemical shift and it is the most commonly used magnetic aromaticity criterion. More precisely, the NICS values are obtained by measuring the ring's current strength when an external magnetic field is applied perpendicularly to the molecular ring. The NICS method is considered as an efficient tool by many researchers since the magnetic properties are most closely linked to aromaticity, because they closely reflect the induced ring currents resulting from the electron delocalization, especially for planar units of similar size [24–29]. Negative NICS values reflect aromaticity, while positive values indicate antiaromaticity [30]. Interested reader will find an excellent review of aromaticity measurements based on magnetic criteria at [12,31].

It is well-known that nitro groups tend to reduce the sensitivity of energetic compounds by drawing electron density from the center of the aromatic ring [32–34]. In the context of energetic molecules, the loss of electron density at the ring center is quantified through the electrostatic potential (ESP) [35–37]. The σ- and π-electron density in the ring center is impacted by electronic properties of the NO_2 groups. Indeed, by replacing a hydrogen atom in the benzene molecule by an NO_2 group, aromaticity is expected to decrease. Moreover, the aromaticity reduction is assumed to be proportional to the number of NO_2 groups added. The aromaticity of energetic molecules is directly related to their sensitivity to detonation. In the field of energetic materials, the design of new materials with adjustable detonation properties is of great importance, where the interest is to combine high performance and low impact sensitivity [38]. However, selecting the best criterion for quantifying slight variations in aromaticity is not a foregone conclusion, and this often produces significantly different findings and misleading chemical interpretations. Choosing the best index to quantify aromaticity remains a tricky subject [13,14,39]. Furthermore, it is not straightforward to select the most relevant index based on merely theoretical arguments. This difficulty to get a single definition is related to the multidimensional character of aromaticity by revealing significant statistical correlations between the different aromaticity criteria [40,41], and to the inherent deficiencies of different indices allowing its quantification [42,43]. Therefore, it is necessary to evaluate aromaticity indices based on several molecular properties to obtain the most comprehensive insight into this property.

In this study, ESP values are used as a reference to quantify the performance of the various aromaticity indices. The ESP is an observable in the quantum-mechanical sense, unlike other indices which are based on mathematical arguments without being measurable quantities. We aim to quantify the slight variations in aromaticity of a set of nitrobenzenes by applying magnetic, electron delocalization, chemical reactivity and information-theoretic approaches, to correlate these criteria-based aromaticity indices with the ESP in the context of energetic molecules.

2. Computational details

All the molecular structures were fully optimized at the B3LYP/6-311++G(d,p) level of theory using the Gaussian 16 W B.01 packages [44]. All NICS calculations have been performed at the M06-HF/cc-pVTZ level of theory. NMR properties calculations are highly dependent on the Hartree–Fock exchange term. In this respect, the Minnesota M06-HF density functional (with 100% Hartree–Fock exchange contribution) [45] is suitable for calculating nuclear magnetic shielding constants [46]. The choice of basis set is also crucial, as the calculation of NMR shielding constants requires at least a triple-ζ quality with at least one set of polarization functions [47]. Additional diffuse functions do not give any improvement of accuracy, only the increase of computational costs. At the same time, additional polarization functions are important. The NICS implementation within Gaussian 16 W B.01 utilizes Gauge-Including Atomic Orbitals (GIAO) [48–50] to compute the nuclear magnetic shielding tensors, which have proven to be particularly accurate for many applications [47,51]. The $NICS_{zz}$ values are computed analogously by using the zz component of the nuclear magnetic shielding tensor in the ring center ($NICS_{zz}(0)$) and 1 Å above the ring plane ($NICS_{zz}(1)$). All NICS indices are based on magnetic criteria of aromaticity. The indices based on electronic delocalization criteria are as follows: the aromatic fluctuation index (FLU) [52], the para-delocalization index (PDI) [53] and the multicenter delocalization index (MCI) [54]. The para-linear response (PLR) indice based on reactivity criteria [55] and the Shannon aromaticity (SA) which is based on the local Shannon entropy concept in information theory [56]. All these indices were calculated by using the Multiwfn 3.8 code [57].

The natural bond orbital (NBO) analysis was performed to quantify the vertical resonance energy (NBO-RE) [58] by using the NBO 6.0 program [59] at the same level of theory. More details on the calculation of NBO-RE are given in ESI (Electronic Supporting Information). In addition, for reproducibility of results, NBO-RE values were calculated with three different density functionals as shown in Table S3 (see ESI). ESP surface maps were run with the Multiwfn 3.8 code from the formatted Gaussian checkpoint file. The corresponding isosurface maps were rendered using the Visual Molecular Dynamics (VMD) program [60]. In addition, a quantitative ESP analysis based on statistical descriptors [61] was performed on the whole molecular surface for each compound.

3. Results and discussion

3.1. ESP analysis

ESP is an observable which can be determined by both experimental and computational methods [62,63]. Conceptually, this scalar field reflects a first-order approximation of the interaction energy at a given point $\mathbf{r}$ in the vicinity of a molecule between the molecular charge distribution (electronic and nuclear) with a unit positive charge located at $\mathbf{r}$ [37]. The ESP is completely defined at every point $\mathbf{r}$ as the sum of the electronic and nuclear charges distributions. Although no polarization occurs during this interaction process, since the molecular charge distribution is not distorted by the external unit charge, the ESP acts as a useful guide for evaluating and predicting the reactivity of molecules towards electrophilic and nucleophilic reactants. It is due to this potential that a molecule is perceived or felt by other chemical entities [64]. From Fig. 1, the ESP is visualized by mapping its values onto the molecular surface according to a color code, where the outer envelope are determined through a constant value of total electron density, $\rho(\mathbf{r}) = 0.001\,a.u.$ Based on the color code considered, regions of negative potential (attractive) appear in red and those of positive potential (repulsive) in blue.

As expected, the ESP of benzene reveals a symmetrical scheme involving negative regions below and above the aromatic ring, caused by the delocalization of π electrons. Positive regions surround the molecule, with surface maxima attributed to the hydrogen atoms. This symmetry pattern is altered as nitro groups are added. Indeed, NO_2 groups exert a strong electron-withdrawing effect, which leads to a depletion of electron density above and below the benzene rings. The presence of NO_2 groups entirely delete the negative regions above and below the aromatic ring, which becomes more positive as the

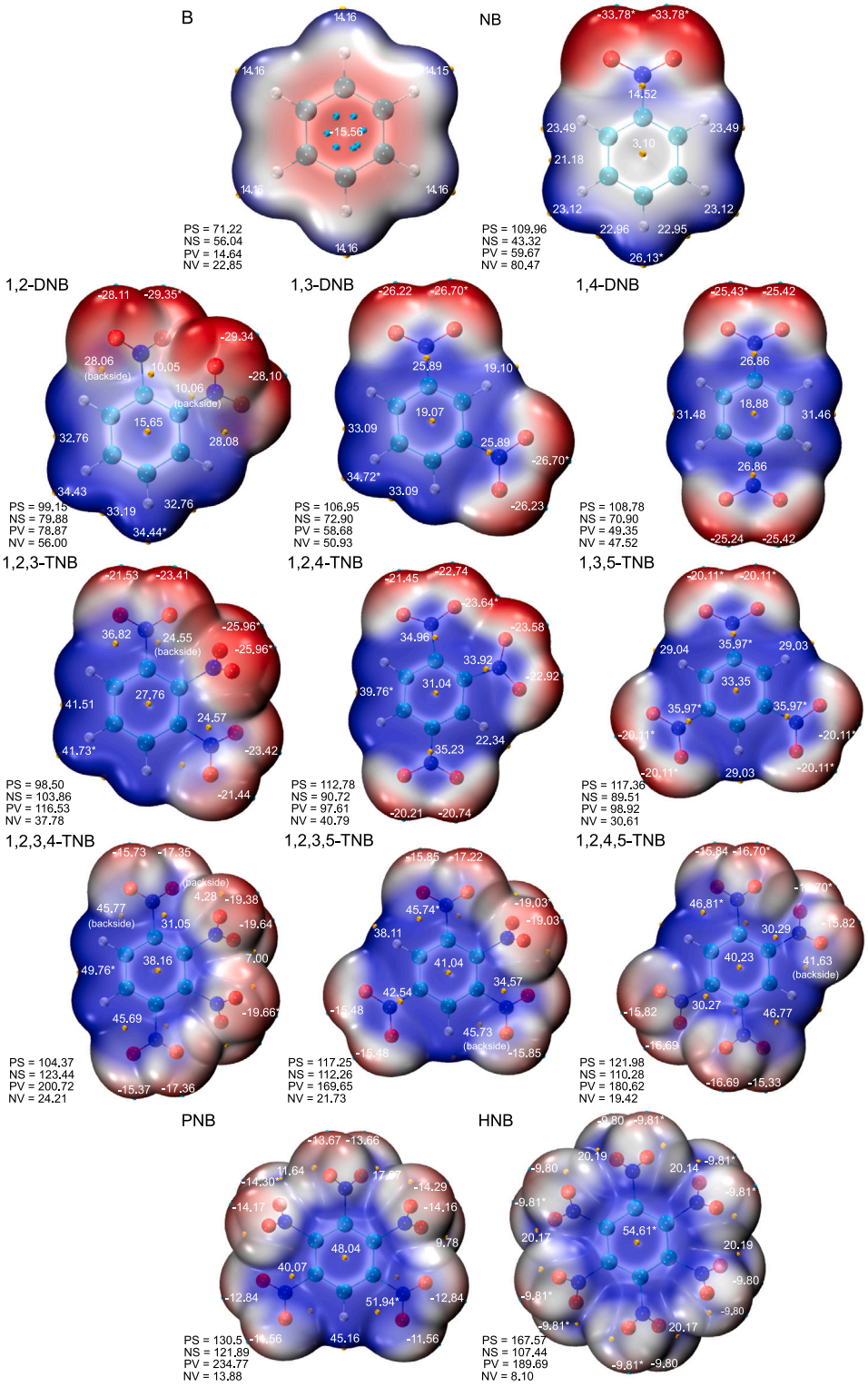


Fig. 1. ESP-mapped van der Waals surface (kcal/mol) using a color scale ranging from red (negative ESP), through white (neutral ESP) to blue (positive ESP). ESP values with a asterisk indicate global surface extreme. The bold numbers in the bottom right-hand corner are the positive ESP variance (PV), negative ESP variance (NV), positive surface area (PS) and negative surface area (NS) whose units are $(kcal/mol)^2$, $Å^2$, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

number of NO_2 groups increases. For instance, with HNB having six strongly electron-withdrawing NO_2 groups, the negative regions in the ring center are severely depleted compared to benzene. Negative ESP values are obtained in the peripheral regions near oxygen and nitrogen atoms, and are attributed to the lone pairs of these heteroatoms. From a local reactivity point of view, these atoms may undergo electrophilic reactions, and the central regions are able to react with nucleophilic reagents. For Benzene, the positive surface is only above the hydrogen atoms. For the other substituted benzenes, the positive surface is mainly located above hydrogen atoms, benzene rings and C-NO_2 trigger bonds,

in which the latter are a key element in the decomposition mechanism of energetic molecules [36,65,66]. In our previous studies [67], we established that intermolecular interactions play an important role in stabilizing the trigger bonds of energetic molecules. The lowest ESP values are found near the regions colored in shades of white, where the molecule is predominantly non-polar.

The positive ESP values in the ring center of energetic molecules are one of the most important parameters influencing their sensitivity towards detonation [38,68,69]. The six NO_2 groups make the benzene ring highly electron-deficient, which is also reflected in the ESP value of the HNB molecule, which is the highest (54.61 kcal/mol) among all the substituted benzenes considered in this study. This is clearly due to the electron-withdrawing effect exerted by the NO_2 substituents, which are more abundant in the HNB ring. In this respect, we can observe a positive correlation between the number of NO_2 substituents and the extent of electron density depletion in benzene ring.

Moreover, it is well known that the NO_2 group disables electrophilic attack on the benzene ring [70]. By examining the ESP of NB, the nitro group generates more partial positive charges at the ortho (23.49 kcal/mol) and para (26.13 kcal/mol) positions, which repel electrophiles, and consequently, this attack is rather oriented towards the meta (23.12 kcal/mol) position. For monocyclic nitrobenzene derivatives with the same number of NO_2 groups, the ESP value at the ring center decreases as the NO_2 groups are more closely spaced. The ESP indicates a value of 15.65 kcal/mol in the center of 1,2-NB, while the ESP reaches a value of 18.88 kcal/mol in the center of 1,4-NB. With a similar trend, the ESP value of 1,2,3-TNB is 27.76 kcal/mol, which is less positive compared to 1,3,5-TNB with the ESP value of 33.35 kcal/mol representing an increase of about 20%. The spatial arrangement of NO_2 groups appears to affect the value of ESP at the ring center, and therefore sensitivity to detonation. The proximity of the NO_2 groups decreases sensitivity to detonation. This can be explained by the strong contribution of Pauli repulsion between the lone pairs of oxygen atoms of two neighboring NO_2 groups, which induces an effect on the π electron rearrangements. Clearly, these intramolecular interactions between NO_2 groups directly affect the π-electron delocalization of the aromatic system. However, a opposite situation is observed for the polycyclic nitrobenzene compounds, where isomers with neighboring nitro groups reveal more positive ESP value in the ring center than isomers with non-neighboring nitro groups [71]. This result is attributed to the aromatic system size. It is also important to emphasize that the ESP values observed around the C-NO_2 trigger bonds are more positive when the NO_2 groups are not adjacent. ESP values near C-NO_2 bond are 10.06 and 26.86 kcal/mol for 1,2-NB and 1,4-NB, respectively. Similarly, ESP values around C-NO_2 bond reach a value of 24.55 kcal/mol for 1,2,3-TNB and a value of 35.79 kcal/mol for 1,3,5-TNB. The activation of the trigger bonds can be caused by an increase in the dihedral angle of NO_2 groups [72].

Positive (PV) and negative (NV) variances quantify the variability of positive and negative surface potentials, respectively. For most organic molecules, the negative variance is much greater than the positive variance [73]. However, the situation is different for nitrobenzene compounds, where we generally observe an inverse pattern, especially for polysubstituted compounds. The NO_2 electron-withdrawing groups induce electron polarization by depleting the central regions of the benzene rings, and significant negative ESP is restricted to the lone pairs of the NO_2 oxygens. This effect is particularly significant when the molecule is polysubstituted. By way of comparison, the contribution of PV to the total variance is about 58.4 and 95.9% for 1,2-DNB and HNB, respectively. This result indicates a large positive charge density fluctuation compared to the negative charge, as the number of NO_2 groups increases.

3.2. Aromaticity analysis

The percentage of variations of the aromaticity indices used to quantify the aromaticity behavior from the viewpoint of magnetic, electronic, chemical reactivity and information-theoretic approaches are summarized in Table 1. The raw values corresponding to the percentages shown in this table are available in ESI (see Tables S1 and S2).

The aromaticity indices at the ring center (NICS(0)) and 1 Å (NICS(1)) above the center of the molecular plane are shown in Table S1. As can be seen from Tables 1 and S1, it clearly appears that the NICS indices show a spatial dependency. As aromaticity decreases, the NICS(0), NICS(1), $NICS_{zz}(0)$ indices are expected to be less negative with respect to benzene. This is not the case, these indices clearly fail to predict the aromaticity of this set of molecules. For instance, the NICS(0) and $NICS_{zz}(0)$ indices predict higher aromaticity values for HNB as compared to benzene, which leads to a counter-intuitive result. The same pattern applies to the NICS(1) index, which predicts a higher aromaticity for 1,2,3,4-TNB than for benzene.

The $NICS_{zz}(1)$ indice exhibits a systematic decrease of aromaticity as more NO_2 groups are added. This component of the shielding tensor corresponds to the principal axis perpendicular to the ring plane, and represents the most appropriate measure of aromaticity when compared with indices derived from the magnetic properties of molecules [74]. This index is the most preferable as it has been shown of being the least contaminated by sources of shielding except the magnetic-induced ring currents [75]. The decrease in $NICS_{zz}(1)$ values can be attributed to the resonance effect, which reduces the delocalization of π electrons, and also to the inductive effect caused by nitro groups, which reduce the charge density above and below the aromatic ring. Indeed, the resonance effect is caused by the conjugation between the ring and the NO_2 group, resulting in the delocalization of π electrons between the ring and NO_2. The inductive effect is due to the withdrawal of σ electrons from the ring to the substituent, since the electronegativity of NO_2 is higher compared to that of the ring carbon. These two concomitant effects reduce the diatropic ring current, which explains the decrease in $NICS_{zz}(1)$ values.

For comparison between closely related chemical structures, it is expected that the σ-bonding contributions to the zz component of the shielding tensor is of the same magnitude. One advantage of $NICS_{zz}(1)$ (this also applies to the other NICS indices) is that its values are easily calculated using commonly available programs and do not require a reference value for the assessment of aromaticity. It is worth mentioning that comparison between NICS values obtained for a set of compounds only makes sense when using the same point of measurement and the same level of theory. Beyond the advantages of NICS indices, the main criticism is that magnetic properties are vector quantities containing all the information about the system. When these properties are represented by a scalar (NICS value), this inevitably leads to a loss of information [76,77]. Additionally, as the magnetic properties are vector quantities, they depend on the position of the compounds with respect to the applied magnetic field. The NICS(0) and NICS(1) indices are calculated from the averaged diagonal components of the chemical shift tensor, and they are therefore heavily contaminated by the σ-electrons from the C–C and C-H bonds. The anisotropic effects are governed by the σ molecular framework [78]. Contamination by these anisotropic effects may explain the poor performance of theses isotropic indices compared to $NICS_{zz}(1)$. The performance of $NICS_{zz}(0)$ is also very poor compared with $NICS_{zz}(1)$, showing that the location of the measurement point in the ring center is crucial.

The location of Bq at 1 Å away from the ring center is much less affected by the transverse components of the chemical shift tensor. As a result, the contribution of the longitudinal component is predominant. In this respect, Schleyer et al. claim that the $NICS_{zz}(1)$ index may be an appropriate alternative for measuring the pure contribution of π-electrons [26].

Table 1
Percentage of variations of indices based on the magnetic, electronic, chemical reactivity and information-theoretic approaches used for the evaluation of aromaticity.

Comp.	$NICS_{zz}(0)$	$NICS_{zz}(1)$	PDI	FLU	MCI	PLR	SA	NBO-RE[a]	ESP[b]
B	100	100	100	99.9	100	100	100	100	0.00
NB	89.84	94.02	92.56	82.89	90.66	91.98	94.80	94.38	26.59
1,2-DNB	96.08	89.36	89.10	67.95	86.56	88.53	90.64	97.29	44.48
1,3-DNB	81.38	89.09	86.83	65.86	84.04	86.01	90.09	94.03	49.35
1,4-DNB	79.87	88.86	88.70	66.06	84.18	89.07	90.09	95.95	49.08
1,2,3-TNB	93.88	85.14	84.80	49.75	81.38	84.22	86.83	81.09	61.74
1,2,4-TNB	86.18	87.07	84.84	52.16	81.11	85.38	86.93	93.75	66.41
1,3,5-TNB	72.36	84.19	82.23	48.52	79.11	81.33	86.37	88.99	69.70
1,2,3,4-TNB	87.82	81.97	81.34	33.76	77.84	82.28	82.90	88.17	76.56
1,2,3,5-TNB	86.49	80.34	80.44	31.63	76.44	79.98	82.78	88.01	80.66
1,2,4,5-TNB	91.86	78.69	81.97	32.74	77.62	81.76	82.75	87.74	79.51
PNB	96.71	76.19	78.54	15.57	73.90	78.45	79.85	87.66	90.64
HNB	99.87	72.17	76.21	0.00	71.21	76.25	77.00	85.77	100.00

IUPAC names and abbreviations of the studied compounds. B: Benzene, NB: Nitrobenzene, 1,2-DNB: 1,2-dinitrobenzene, 1,3-DNB: 1,3-dinitrobenzene, 1,4-DNB: 1,4-dinitrobenzene, 1,2,3-TNB: 1,2,3-trinitrobenzene, 1,2,4-TNB: 1,2,4-trinitrobenzene, 1,3,5-TNB: 1,3,5-trinitrobenzene, 1,2,3,4-TNB: 1,2,3,4-tetranitrobenzene, 1,2,3,5-TNB: 1,2,3,5-tetranitrobenzene, 1,2,4,5-TNB: 1,2,4,5-tetranitrobenzene, PNB: Pentanitrobenzene, HNB: Hexanitrobenzene.

[a] NBO-RE: Natural Bond Orbital Resonance Energy, known as vertical resonance energy.

[b] The ESP value in the ring center. ESP values are provided for comparison purposes.

The PDI index not only shows a decrease in aromaticity as the number of NO_2 substituents increases, but also a relatively high sensitivity for discriminating aromaticity between the different isomers. For instance, 1,3-DNB is less aromatic than the other dinitrobenzenes. Similarly, 1,3,5-TNB and 1,2,3,5-TNB are less aromatic among the trinitrobenzenes and tetranitrobenzenes, respectively. Similar performance is obtained with MCI, showing an aromaticity reduction percentage analogous to that of PDI. A main weakness of PDI concerns its limitation for estimating only the local aromaticity of six-membered rings. MCI is a very popular index for assessing local and global aromaticity. In current version of Multiwfn code, the MCI index requires a calculation time increasing linearly with the molecular size, which is a real advantage. The FLU index is able to predict slight variations in aromaticity, indicating relatively high sensitivity. FLU is derived from the delocalization index (DI) by measuring divergences (DI differences for each single pair bonded) from aromatic molecules chosen as a reference. Its advantage lies in its ability to be used to describe rings with any number of atoms. However, its dependence on reference values is one of the principal drawbacks of this index.

Although the PLR index predicts almost identical aromaticity for the 1,2,4,5-TNB and 1,3,5-TNB isomers, it remains relevant for predicting small variations in aromaticity of the other isomers. Furthermore, when examining the percentage of changes in aromaticity, similarities appear between the PLR and PDI indices. This result is expected, since the definition of para linear response index (PLR) has an analogy to PDI. Geerlings et al. claim that PLR is as useful as PDI in quantitatively measuring aromaticity as the two indices show a strong linear correlation [79]. The SA index predicts a decrease in aromaticity as the number of NO_2 groups is increased. However, this indice based on the information-theoretic concept fails completely to predict the aromaticity differences between the isomers. The SA index is not efficient to distinguish slight changes in aromaticity for the investigated compounds. The MCI, PDI and FLU indices based on electron delocalization criteria seem more sensitive for discriminating small variations in aromaticity in di–, tri– and tetranitrobenzene isomers.

Overall, the NBO-RE values clearly show a systematic reduction of aromaticity as nitro groups are added, indicating that NO_2 group acts as a ring deactivator. For instance, the NBO-RE of HNB exhibits a percentage reduction of aromaticity of about 14.2% compared to benzene. However, despite the replacement of six hydrogen atoms by NO_2 groups, benzene exhibits a strong resistance of its aromatic system to disrupt the π-electron structure. This result confirms that the aromaticity of benzene rings is quite robust, and highlights the propensity of aromatic systems to preserve their initial π-electronic structure along the reaction course, leading to aromatic substitution [80]. Moreover, the NBO-RE was unable to describe properly the aromaticity between NB and 1,2-DNB, where the latter is expected to be less aromatic. The visualization of the correlation matrix is depicted in Fig. 2. Taking the ESP values obtained at the ring centers as reference, the best correlations are observed with MCI ($r = -0.996$), PDI ($r = -0.994$), PLR ($r = -0.985$); $NICS_{zz}(1)$ ($r = 0.979$) and FLU ($r = 0.977$). The lowest correlations are observed with NICS(1) and $NICS_{zz}(0)$. One should beware of the false correlation between NICS(0) and ESP. NICS(0) is supposed to correlate positively with ESP, but this is not the case. This index completely fails to describe aromaticity, since it predicts an increase in aromaticity as the number of NO_2 groups increases. This result is obviously counter-intuitive and reflects the conceptual limitations inherent in this index. The other aromaticity indices showed intermediate performances.

These results indicate that the most suitable aromaticity index is not based on a single criterion, and that selecting it is more subtle. There is no single way to assess aromaticity, most likely because each criterion fails to consider all the phenomena inherent to aromaticity. Accordingly, it is important to combine information from several criteria to obtain a more complete description of the aromaticity of the studied compounds.

4. Conclusion

Benzene exhibits a larger electron density in the ring center, unlike other substituted nitrobenzenes. Indeed, the ESP reveals that the nucleophilic character in the ring center of benzene disappears and becomes electrophilic for nitrobenzene compounds. The presence of electron-withdrawing NO_2 groups linked to the benzene ring attracts the π cloud towards them, producing a positive hole above and below the aromatic ring. This effect is particularly important as the number of nitro groups increases. The ESP of nitrobenzene compounds clearly shows how substituents affect the reactivity of aromatic systems. In this respect, ESP can be viewed as a local hardness indicator.

As mentioned above, the NICS method is widely used within the theoretical chemistry community. In this regard, it is essential to identify the most appropriate NICS index describing the degree of aromaticity. According to our results, among magnetic-based indices, only $NICS_{zz}(1)$ is capable of properly predicting small changes in aromaticity. This out-of-plane component is less sensitive to local induced fields originating from the core and localized electrons such as lone pairs and sigma bonds. These local magnetic fields are expected to be short-range, vanishing as one moves away from the ring center. Electron delocalization indices (PDI, MCI and FLU) proved to be more sensitive for describing the degree of aromaticity of monocyclic nitrobenzene compounds. The

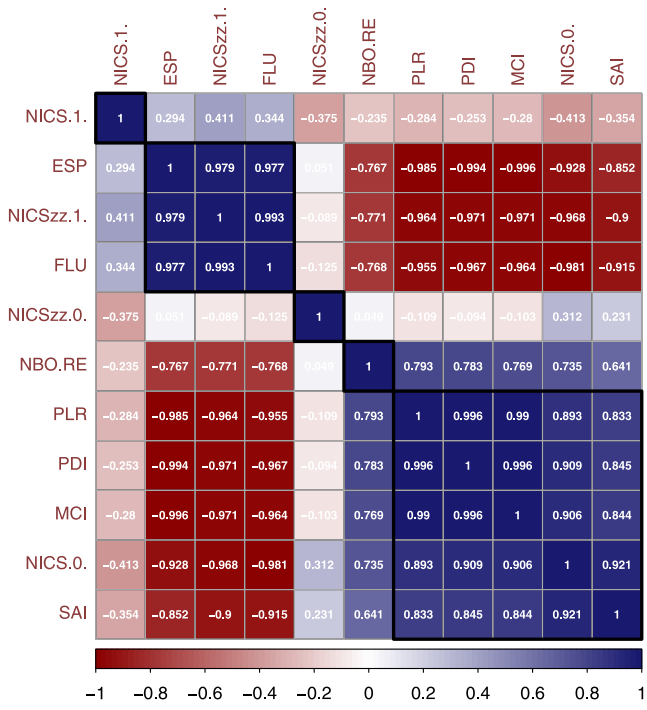


Fig. 2. Graph of the correlation matrix. Positive and negative correlations are displayed in blue and red color, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

SA indice based on the information-theoretic concept fails completely to predict the aromaticity between the isomers. Besides, the PLR index based on the reactivity criteria derived from conceptual DFT, performs much better. From benzene to HNB, the loss of benzene ring stability assessed by NBO-RE is relatively low (14.2%). Benzene exhibits a strong resistance of its aromatic system to disrupt the π-electron structure, confirming that the aromaticity of benzene rings is quite robust.

From the results obtained, the most appropriate aromaticity index is not based on a single criterion. There is no single way to assess aromaticity, most likely because each criterion fails to consider all the phenomena inherent to aromaticity. It is therefore important to cross-check the information from several criteria in order to achieve a more comprehensive description of aromaticity of the studied compounds.

CRediT authorship contribution statement

Samir Kenouche: Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Nassima Bachir:** Visualization, Validation, Software, Methodology. **Wissam Bouchal:** Visualization, Validation, Software, Formal analysis, Data curation. **Jorge I. Martínez-Araya:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.jmgm.2024.108728.

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