**Bonding, Aromaticity and Isomerization of Furfuraldehyde through Off-Nucleus Isotropic Magnetic Shielding**

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### 1. Introduction

Aromaticity and bonding are among the most widely used concepts in chemistry. Yet, there has been no experimental method able to assess aromaticity. Some alternative theoretically based methods have been used for this purpose. Perhaps the simplest one is known as the “Hückel rule” which counts $(4n + 2)$ electrons. However, the term “aromaticity” is much more problematic since it is associated with an array of variables. It is widely accepted that aromaticity can best be measured through electronic, geometric, energetic and magnetic criteria. Among these criteria, the magnetic criterion is preferable since it emerged from ring current and electron delocalization that uniquely occurs in an aromatic ring.

Nuclear magnetic resonance (NMR) is an important aspect of the magnetic criterion. According to NMR theory, when a molecule is exposed to an external magnetic field (B$_{0}$) any nucleus K of the molecule will experience an amount of magnetic field (B$_{K}$). This can mathematically be expressed as shown in Equation (1):

$$B_{K} = B_{0}(1 - \sigma_{K})$$  \hspace{1cm} (1)  

where $\sigma_{K}$ is the chemical shielding tensor of the nucleus K which can be obtained from a 3×3 matrix. Relevantly, the average of the trace of the matrix gives the nuclear isotropic magnetic shielding ($\sigma_{iso}$) of the nucleus K.

Although $\sigma_{iso}$ can be obtained from both experimental and theoretical means, the magnetic off-nucleus shieldings $\sigma(r)$ as well as the isotropic magnetic shielding ($\sigma_{iso}(r)$) in spaces at a distance (r) from the nucleus is still an exclusive feature of quantum chemical methods. Off-nucleus shieldings were first reported in 1958 by Johnson and Bovey who documented the chemical shift values for spaces surrounding benzene.

In one of the most significant works on off-nucleus shielding calculations, Schleyer et al. assessed aromaticity through a new index called nucleus-independent chemical shift (NICS). NICS (or NICS(0)) is a reversed sign of the single value of the isotropic shielding, that is, $-\sigma_{iso}(0)$, which is probed from the point $r_0$ that locates at the center of the ring plane of monocyclic or polycyclic systems.[5–9] When the point locates at 1 Å vertically above the ring center, that is, at $r_1$, NICS in this case can equally be written as NICS(1). Negative NICS values refer to aromatic molecules, whereas antiaromatic rings are associated with positive NICSs. Schleyer and co-workers recommended using NICS(1) instead of NICS(0) because the former prevents errors that arise from local interferences at the NICS(0) region.[10,11] However, some debates on the NICS technique conclude that representing multifold molecular properties through a single-point NICS index is not always adequate.[12,13] Hence, understanding molecular chemical shielding has advanced through developing the isotropic shielding calculations to perform calculations for a multidimensional array of points instead of only for a few dimensionless points. The possibility of using a one-dimensional (1D) layout of points is an example of such developments that allows scanning the magnetic shielding along a straight line within the molecular space.[14–16] Significant efforts have focused on utilizing 2D and 3D magnetic shielding.

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/open.202100202  
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calculations. Some preliminary work was carried out by Kleinpeter and Klod to explore the 3D isotropic shieldings for some cyclic and acyclic molecules.11

Their work mainly depended on using 0.5 Å spacers among evenly distanced points to form regular 3D grids of points. They represented the obtained magnetic responses as isochemo shielding surfaces (ICSS)17 that helped to reveal molecular magnetic properties of a wide range of molecules.18–21

Karadakov and Horner made further improvements by employing finer spacers of 0.05 Å rather than 0.5 Å to detail furfuraldehyde (FD). This modification has allowed better exploration of the bonding and aromaticity of a wide range of molecules. For example, calculations on benzene, cyclobutadiene and $S_2N_2$ in their ground20,22 and some excited states21,23 besides some acyclic hydrocarbons26 have been reported.

Yet, investigating the isomerization through multi-dimensional $\sigma$ iso($r$) calculations has not been covered in the literature. Therefore, we have been investigating the isomerization of some aromatic molecules. The present paper details bonding and isomerization of one of them, furfuraldehyde (FD), see Figure 1, for which very little published experimental and theoretical magnetic data has been reported.21,22 Since the magnetic behaviors directly depend on the chemical and magnetic environments of the atoms in these two groups. No clear explanations can be found for the variation in $\sigma$ iso($r$) for any specified nucleus in the three forms of FD (Table 1).

However, there are some clues about the impacts of FD isomerization on $\sigma$ iso($r$) values. For example, $\sigma$ iso($r$) values of hydrogen nuclei are less influenced by the isomerization with a difference of circa 1 ppm. However, when comparing $\sigma$ iso($r$) responses for cis and trans, it can be seen that $H_5$ and $H_7$ exhibit lesser differences in $\sigma$ iso($r$) than $H_3$ and $H_5$. Juchnovskii and Kaneti observed a similar trend of variation.27 The carbon and oxygen nuclei of the furanyl ring show more differences in $\sigma$ iso($r$) of around 4–18 (ppm). The highest variations in $\sigma$ iso($r$) are found for $C_6$ (≈21 ppm) and $O_2$ (≈150 ppm) of the formyl group. Thus, the above variations may arise from the dependency of $\sigma$ iso($r$) on the functional group rotation about the C$_2$–C$_6$ bond of FD.28

2. Results and Discussion

2.1. Nuclear Isotropic Shieldings

Table 1 lists the nuclear isotropic shieldings $\sigma$ iso($k$) of the nuclei of the three FD forms. These values were collected from the output files after the completion of $\sigma$ iso($r$) GIAO-B3LYP/6-311 + G(d,p) calculations. According to Table 1, the carbon and oxygen atoms of furanyl have $\sigma$ iso($k$) values different from those of the formyl group. Fewer differences exist between $H_3$, the aldehydic hydrogen, and the hydrogen atoms of the furanyl ring (H$_5$, H$_7$, H$_8$). It seems possible that these variations in the $\sigma$ iso($k$) values are caused by the dissimilarity between the chemical and magnetic environments of the atoms in these two groups.

2.2. Off-Nucleus Isotropic Shielding: A General Overview

Figures 2–4 show the overall 2D and 3D $\sigma$ iso($r$) responses of cis, TS and trans FD. Two colors, blue and red, respectively, represent the responses of shielding (+ $\sigma$ iso($r$)) and deshielding (− $\sigma$ iso($r$)) activities. Saturation levels of these two colors are functions of the strength of the above-mentioned two magnetic activities. Since the Z-axis is set perpendicular to the FD plane (Figure 5), the axis has the same orientation in the contour maps of Figure 2. Maps a to e of Figure 2 therefore illustrate the 2D $\sigma$ iso($r$) responses respectively at $z = 0.00$, 0.25, 0.50, 0.75 and 1.00 Å above the FD nuclear level. It is clear that local deshieldings spherically surround carbon and oxygen nuclei (see red clouds in maps a and b of Figure 2). We termed each of these deshieldings ‘deshielded sphere’ (DS). DS have been described as a magnetic feature of $\pi$-electron movements of the second-row atoms with sp2 hybridization.21,24,29,30 DSs of FD possess an approximate radius of less than 0.50 Å, which then fade away beyond this distance limit (see maps a and b and compare them with maps c–e in Figure 2). The DSs sizes of the carbon and oxygen nuclei are smaller in the furanyl ring than those in the formyl group. DSs follow the size order of O$_1 < C_1 < C_2 < C_3 < C_5 < O_2 < C_6$.

Since the magnetic behaviors directly depend on the electron charge movements, it is likely that long-range electron

![Figure 1. Atoms labelling and numbering scheme of cis and trans isomers of furfuraldehyde (FD).](image)

| $\sigma$ iso($k$) | cis | TS | trans |
|------------------|-----|----|-------|
| $C_1$            | 22.021 | 24.515 | 20.819 |
| $C_2$            | 55.152 | 73.330 | 62.535 |
| $C_3$            | 66.521 | 68.178 | 65.240 |
| $C_4$            | 29.090 | 35.166 | 30.175 |
| $C_5$            | 5.197 | 6–311+ | 0.500 |
| $C_6$            | 22.466 | 22.958 | 16.757 |
| $C_7$            | −296.183 | −444.523 | −294.153 |
| $H_1$            | 24.877 | 25.588 | 24.470 |
| $H_2$            | 25.372 | 25.449 | 25.303 |
| $H_3$            | 24.167 | 24.400 | 24.272 |
| $H_4$            | 22.052 | 20.900 | 21.818 |

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movement profiles that generate $\sigma_{iso}(r)$ are dissimilar in the shielded regions (the blue zones) than in the deshielded sectors (the red spheres; see Figures 2–4). However, the association between shielding and deshielding activities requires more research to be more precisely understood.

Maps a–e of Figure 2 show that shielding and deshielding activities at different vertical heights above the FD plane can help to scan molecular magnetic activities from $\sigma$ to $\pi$ regions. This technique is in accordance with that used in the works of Schleyer and co-workers who recommended probing shielding values mainly from the $\pi$ region besides the $\sigma$ region (as NICS(1) and NICS(0), respectively) when assessing the magnetic criterion of aromaticity.\(^{[10,11]}\)

Most of the observable magnetic features of Figure 2 can also be seen in the 3D $\sigma_{iso}(r)$ responses (Figure 3). Four isosurfaces were visualized in Figure 3 to make the overall isotropic magnetic shielding behaviors more understandable. The blue and the transparent white isosurfaces illustrate the shielding values of $\pm 15$ and $\pm 8$ ppm, respectively, whereas the red and transparent red isosurfaces, respectively, represent deshielding values of $\pm 16$ and $\pm 3$ ppm. The blue isosurface occupies spaces close to FD nuclei, whereas the transparent white isosurface prefers to occupy farther regions. Therefore, higher magnetic shielding activities prefer closer locations to the molecular structure. The red and transparent red isosurfaces show that the shapes of DSs of the nuclei in the furanyl ring are almost equivalent. These DSs are dissimilar to those DSs of the

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**Figure 2.** Isotropic shielding $\sigma_{iso}(r)$ contour maps (in ppm) for cis (left), transition state (TS) (middle) and trans (right) forms of furfuraldehyde (FD) calculated by placing five 2D grids of bq atoms at 0.00, 0.25, 0.50, 0.75 and 1.00 Å above the FD molecular plane, (a) to (e), respectively. The calculations were performed using DFT-GIAO level/B3LYP functional and 6-311 + G(d,p) basis set.
and O atoms of the formyl group, which may also result in a further variation between the magnetic environments of these two groups.

An effort has been made to compare multidimensional $\sigma_{iso}(r)$ values (Figures 2 and 3) with total electron density $\rho(r)$ (Figure 6). Unlike the previous discussion of the 2D and the 3D $\sigma_{iso}(r)$ values that detailed a wide range of structural features, the $\rho(r)$ representations in Figure 6 are limited to display fewer details. For example, double bonds, electron lone pair regions and electron-rich atoms like oxygen can be seen through the $\rho(r)$ value of 0.3 a.u. One reason behind this is that $\rho(r)$ rapidly decreases when going outside the nucleus. In this context, a

Figure 3. Isotropic shielding $\sigma_{iso}(r)$ isosurfaces for cis (left), transition state (TS) (middle), and trans (right) forms of furfuraldehyde (FD) calculated by employing 3D grids of bq atoms. (a) Side views, (b) top views and (c) cross-sectional views. The isosurfaces were obtained from DFT-GIAO calculations using the B3LYP functional and the 6–311 + G(d,p) basis set. The isosurface color/$\sigma_{iso}$ (ppm) are blue/+15, transparent white/+8, red/-16 and transparent red/-3.

Figure 4. DFT-GIAO/6-311 + G(d,p) isotropic shielding $\sigma_{iso}(r)$ contour maps (in ppm) for the C$_4$C$_5$ (a and b) and C$_2$C$_6$ (c and d) bonds of cis, maps (1), transition state (TS), maps (2), and trans, maps (3), furfuraldehyde (FD). Maps (a) and (c) are cross-sectional views, whereas (b) and (d) show the cross-sections along the bonds. Note that the well-shielded black dots at the left and right sides of the origin point represent the nuclei centers of C$_4$ and C$_5$ in maps (b) and C$_2$ and C$_6$ in maps (d). Also, the origin point in each map corresponds to the bond midpoint.
common feature can be seen between $\sigma_{iso}(r)$ and $1(r)$ activities when they become weaker at distant spaces surrounding FD. The transparent white isosurface of $\sigma_{iso} = +8$ ppm in Figure 3 almost shares the same space occupation around FD like the blue isosurface of $1(r) = 0.1$ a.u in Figure 6. However, both these isosurfaces can give a general idea about these parameters without supplying sufficient structural details. Similar trends of the advantages of $\sigma_{iso}(r)$ over $1(r)$ have also been reported for some acyclic hydrocarbon molecules.\(^{24}\)

2.3. Bonding in Furfuraldehyde

If we consider that the electron patterns at the $\pi$ and $\sigma$ regions are responsible for the $\sigma_{iso}(t)$ behavior at these two regions, tracing the corresponding $\sigma_{iso}(t)$ responses may reveal several electron-related features such as bonding and electron delocalization. On this basis, we specified Figure 2 to scan the isotropic shieldings at five vertical heights (between 0.00–1.00 Å) that extend from $\sigma$ to $\pi$ regions.

The blue shielding clouds ($+\sigma_{iso}(r)$) about FD bonds in contour maps a–c magnetically construct the shapes of C–H, C–C and C–O bonds. At these three heights, that is, 0.00, 0.25, and 0.50 Å, the blue shielding clouds about the bonds mainly correspond to FD $\sigma$-bonding and partially to $\pi$-bonding, and vice versa for maps d and e that are located at 0.75 Å and 1.00 Å, respectively. The strongest bond in shielding is C–O, followed by C–C, while C–H is the weakest.

The shielding clouds about the C–O bonds are possibly not solely constructed by the bonding between carbon and oxygen of C–O bonds. Oxygen electron lone pairs most probably take part in the magnetic activity locally about oxygen atoms and broadly at the spaces surrounding the C–O bonds. Take, for example, the case of O$_1$ in maps a–c of Figure 2. The shielding clouds around the C$_1$–O$_1$–C$_5$ bonds are integrated into one triangular cloud. Maps c and d show
localized shielding islands above O₅ and O₇ which may be formed by the actions of the electron lone pairs of oxygen. Similar shielding trends exist around the heteroatoms of some heteroaromatic rings.[31]

The inhomogeneous distribution of the shielding cloud about the C₄–O₅ bond is noteworthy. A remarkable polarization in the shielding cloud towards the O₅ atom can be seen in Figures 2 and 3. In comparison, a lower polarization towards O₇ can also be observed for the C₇–O₇–C₈ bonds. It is a fact that the electronegativity values of oxygen and carbon are unequal. The electronegativity difference is the main reason for this kind of polarization. As a result, in a polarized bond, the DS size of the lower atom in electronegativity may become much larger than that of the same type of atom in homoheteroatomic bonds. For example, the DSs of C₆, C₇, and C₈ are bigger than the DSs of C₃ and C₄. It was found that different types of atoms in a ring cause the bonds to be polar since the polarized electrons become localized[30] not only in organic rings but also in some hetero-inorganic analogues of benzene.[32]

The regions near and at the midpoints of the C–C bonds display more shieldings than spaces in the vicinity. Making a simple comparison among the C–C bonds indicates that the spaces at and around the C₄–C₅ bond have the lowest \( \sigma_{iso}(r) \), in particular for the TS (see the bond in Figures 2 and 3). In contrast, C₂–C₃ and C₄–C₅ have the strongest shieldings (see maps c in Figure 2). This behavior is similar to that observed in the furan ring that reflects the double bond character of these two bonds.[30]

To detail the variations in the isotopic shieldings between the cyclic and acyclic C–C bonds of FD, two types of grids (see Figures 5d and 5e) were used to compare two selected bonds, \( C_4-C_5 \) and \( C_5-C_6 \), as cyclic and acyclic bonds, as shown in Figure 4. The symmetry of shielding distributions about the center of the \( C_4-C_5 \) bond in contour maps a and b in Figure 4 is similar to that found in C–C bonds of aromatic molecules.[31] In contrast, the irregular and asymmetric shielding distributions in maps c and d of Figure 4, respectively, show a narrowing in the width of the shielding cloud besides a shifting in the shielding cloud from the bond midpoint towards \( C_5 \) of the \( C_4-C_5 \) bond. Therefore, one can say that considering the type of bond in the isotopic shielding evaluations is not sufficient without considering the effects of the surrounding magnetic and electronic environments of that bond.

To obtain numerical shielding responses along bonds, 1D grids, like that shown in Figure 5b, were set along each bond of FD. The \( \sigma_{iso}(r) \) responses from these grids have been plotted in Figure 7. We found that the \( C_4-C_5 \), \( C_5-C_6 \) and \( C_4-C_6 \) bonds have the maximum \( \sigma_{iso}(r) \) values at their bond midpoints of around 40 ppm with superiority for \( C_4-C_5 \) over other bonds, see curves (i), (iii) and (iv) of Figure 7, whereas about half of these shielding values, \( \approx 20 \text{ ppm} \), is found at the midpoint of the \( C_4-C_5 \) bond (curve (ii) in Figure 7). The electron-withdrawing effects of the CHO group may cause electron deficiency in the \( C_4-C_5 \) bond.

When considering only the positive \( \sigma_{iso}(r) \) values, that is, without the negative \( \sigma_{iso}(r) \) values of the DSs at bond terminals, the regions at and near the bond midpoints of \( C_4-C_5, C_5-C_6 \) and \( C_4-C_6 \) bonds show nearly no shielding polarization, see curves (i), (iii) and (iv) of Figure 7. The absence of a significant difference in electronegativity between the two nuclei of a homonuclear bond causes no bond polarization. Significant polarization in the peaks towards oxygen atoms of the heteronuclear \( C_4-O_5 \) and \( C_5-O_6 \) plots is observable, see curves (v) and (vi) of Figure 7, respectively. Less polarization in shielding for the \( C_4-O_5 \) bond can be seen in curve (vii) of Figure 7 since its polarization mainly occurs at higher vertical heights above the bond, that is, at the \( \tau \)-region. Hence, the 2D maps in Figure 2 and the 3D isosurfaces in Figure 3 clearly show this issue. All four \( C-H \) bonds share almost the same shielding pattern, see curves (viii)–(xii) in Figure 7. However, some remarkable differences are recognizable among them. The highest shielding value at the bond midpoints of these bonds is \( \approx 26 \text{ ppm} \) for \( C_4-H_5 \) followed by \( \approx 25 \text{ ppm} \) for \( C_5-H_6 \) and \( \approx 20 \text{ ppm} \) for the \( C_6-H_7 \) bond, whereas the \( C_7-H_8 \) bond has the lowest value of \( \approx 5 \text{ ppm} \). These variations could be considered as a normal subsequence of the variations in the surrounding environment and the \( C-H \) location of these bonds to which group the \( C-H \) bond may be linked.

2.4. Aromaticity in the Furanyl Ring

Unsubstituted furan is a heterocyclic aromatic molecule that satisfies the \( \pi \)- sextet rule. Four \( \pi \) electrons from the carbon atoms and two \( \pi \) electrons from the oxygen atom make furan owns six \( \pi \) electrons. The isotropic shieldings at the \( \pi \) region of furanil in Figure 2 are like those of furan in ref. [29]. Contour lines of 15 and 10 ppm, respectively, in maps d and e of Figure 2 form a pentagonal-shaped shielding cloud above the five nuclei of the furanyl ring frame. The pentagonal clouds most probably relate to the \( \pi \) electron circulation and the ring current at the \( \pi \) region. Hence, one may conclude that the \( p_\pi \) electron delocalization prefers heights around 0.75 to 1.00 Å above the furanyl plane. The overall 2D \( \sigma_{iso}(r) \) magnetic activity about furanyl shows almost no significant dependency of \( \sigma_{iso}(r) \) of the ring on the isomerization (see and compare the last six maps d and e in Figure 2). However, some differences are noticeable from the NICS(0–2 Å) curves (plot (xii) in Figure 7), that are obtained from employing 1D grids similar to that shown in Figure 5c.

TS FD and furan show the largest NICS(0-2 Å) values located at their ring centers. This behavior may suggest that both furan and TS FD possess a sort of in-plane aromaticity. This type of aromaticity exists when the maximum ring current, and consequently the magnetic shieldings, are located at the ring plane rather than above or below the ring plane.[33] The similarities between the NICS(0−2 Å) curves of furan and TS FD may be attributed to the breaking in the \( \pi \) electron delocalization over the rotated \( C_4-C_5 \) bond in TS FD, see also the \( \sigma_{iso}(T) \) maps of this bond in Figure 4. Hence, the furanyl ring holds its \( \pi \) electrons and involves them in the \( \pi \) electron circulation within the furanyl ring region, like that of unsubstituted furan.
Based on NICS(0-2 Å) curves in the plot (xii) of Figure 7, the shielding is almost constant at heights higher than 0.8 Å above the ring centers for all the studied structures. We, therefore, can say that the isotropic shieldings at \( \pi \) regions around this height have less dependency on isomerization. Finally, according to NICS(0–2 Å) curves, the degree of aromaticity follows the arrangement TS FD > furan > trans FD > cis FD.

2.5. The Isomerization Impacts on the Isotropic Shieldings of FD

Each bond of furfural is represented in Figure 7 by three curves which belong to \( \sigma_{\text{iso}}(r) \) of the bond in cis, TS and trans FD, respectively. The smallest \( \sigma_{\text{iso}}(r) \) variation is found between the cis and the trans isomers. Also, the red curves in plots (i)–(x) of Figure 7 show that TS FD is accompanied by a lowering in \( \sigma_{\text{iso}}(r) \) for the bonds outside the furanyl ring (see curves (ii), (vii) and (xi) in Figure 7), whereas \( \sigma_{\text{iso}}(r) \) for the bonds of furanyl either increased or remain unchanged.
To provide a better understanding of the variation in $\sigma_{iso}(r)$ between cis and trans FD, the differences in the isotropic shieldings along each bond in these two forms, $\Delta \sigma_{iso(cis-trans)}$, are represented in Figure 8.

The three plots of Figure 8 specify three groups of bonds, that is, C–C, C–O, and C–H. Negative $\Delta \sigma_{iso(cis-trans)}$ values mean that the shielding for a bond is higher in the trans form and vice versa. $\Delta \sigma_{iso(cis-trans)}$ values vary within a range of approximately ±8 ppm. In more detail, the C–O–C bonds show the highest variations (Figure 8b). In contrast, shielding along the C–C bond is almost constant (Figure 8a). The middle parts of the curves near bond midpoints of C–C, C–C, and C–O1 possess higher shieldings in the trans form, whereas C–O1 shows an opposite trend. Fluctuations in the shielding along the bonds of the formyl group, that is, C–C and C–O, are noticeable.

No significant $\Delta \sigma_{iso(cis-trans)}$ occurs at regions closest to the hydrogen atoms (Figure 8c). In contrast, the parts near the bond midpoint show slightly more shieldings for the C–H and C–H bonds in cis FD and C–H and C–H bonds in trans FD.

Figure 4 shows some notable points about FD isomerization. During the isomerization, the lowest difference in $\sigma_{iso}(r)$ is found for C–C. In comparison, C–C shows unusual variations in $\sigma_{iso}(r)$ since it undergoes a rotation (see maps c and d in Figure 4). In more detail, for C–C, no significant differences in $\sigma_{iso}(r)$ were found in Figure 4 between the cis (maps c1 and d1) and the trans (maps c3 and d3) isomers, whereas $\sigma_{iso}(r)$ becomes remarkably weaker and much more inhomogeneous in TS FD, (see maps c2 and d2 in Figure 4). Interestingly, the cross-section shows the shielding cloud of the C–C bond in TS FD has a horizontal alignment along the x-axis (see map c2 in Figure 4). In contrast, the same bond has vertically aligned shielding clouds in cis and trans FD as respectively illustrated in maps c1 and c3 of Figure 4. Thus, the structural changes affect the isotropic shieldings, which seems likely owing to the dependency of $\sigma_{iso}(r)$ on the profiles of electron and orbital orientations of the isomers.

### 3. Conclusion

Multidimensional off-nucleus isotropic magnetic shieldings $\sigma_{iso}(r)$ at the DFT-GIAO B3LYP/6-311 + G(d,p) level of theory showed a good capability of evaluating different structural aspects. This included bonding, aromaticity and the isomerization of furfuraldehyde (FD). In comparison, both electron density $\rho(r)$ and nuclear magnetic shieldings $\sigma_{iso}(k)$ neither completely detailed the structural features of FD nor accurately designated the effects of FD isomerization from cis to trans. Scanning the shieldings at different heights above the molecular plane revealed some noteworthy points. For instance, in regions from the FD molecular plane up to heights less than 0.5 Å above the FD plane, the shielding activities of $\sigma$-bonding and DSs can be observed. Contrary, the shieldings at a vertical height between 0.75 to 1.00 Å above the FD plane showed features of $\pi$-bonding and $\pi$ electron delocalization activities.

Among C–C bonds, the C–C bond is the strongest in isotropic shielding content. The isotropic shielding distribution around this bond showed a high level of symmetry. Contrary, the C–C bond is the weakest and has unusual and irregular shielding clouds in all three FD forms.

Noticeably, the electronegativity difference between carbon and oxygen may play a key role in the shielding behavior of the C–O–C bond. Subsequently, we found significant polarization in the isotropic shielding clouds towards the oxygen of these bonds.

The isomerization affects the isotropic shieldings of the formyl group more than the furanly ring. Also, the C–H bonds showed the lowest dependency on the conformational changes, whereas the C–C bond showed the highest variation in its shieldings during the isomerization due to the bond rotation at this bond.

Interestingly, in the TS form, the isotropic shieldings for the bonds of furanary increased or remained the same during the isomerization. In contrast for the formyl group, the bonds showed a decrease in their shieldings.

One can describe the isotropic shieldings and deshieldings as two opposite magnetic activities. In addition, the shieldings and deshieldings activities behave differently in the furany and formyl entities. The differences in DS shapes and the shielding

![Figure 8](image-url)
clouds distribution about the bonds reflect the difference between these two activities. The NICS(0-2 Å) index classified the furanyl group as aromatic in all three FD forms. However, the center of the furanyl ring plane in TS has a marginally more negative NICS value than found for the cis and trans FD forms or even in furan. Based on the NICS(0-2 Å) index values, the aromaticity of the above structures follows the arrangement of TS > furan > trans FD > cis FD.

Finally, Δσ(niso-trans) and other 1D curves showed finer numerical details along the FD bonds.

**Computational Method and Procedure**

To optimize the three forms of gas-phase FD, that is, cis, TS and trans FD, besides estimating their vibrational frequencies, density functional theory (DFT) was employed under the B3LYP functional and 6-311 + G(d,p) basis set. The optimized geometries were then involved in all of αα(r) calculations. Gauge-including atomic orbitals (GIAO) as a method for molecular orbital expansions at the same level of the theory mentioned above was involved in αα(r) calculations. All the calculations of this work were carried out by Gaussian09 software package.141

According to the Gaussian program, some physical properties, including αα(r), can be locally probed through one or more virtual atoms which are called “ghost atoms” and are symbolized as “bq”. Therefore, the aim of this work was approached by utilizing one- to three-dimensional (1D-3D) grids of bq. However, placing too many points of bq at pre-specified locations somewhere around the molecular geometry are subject to two constraints. The first is the limitation of the Gaussian application of caring out a large number of bq. The second is to find a way to specify the spatial placements of bq as (x,y,z) Cartesian coordinates to be regularly placed in the selected pattern of the multidimensional grids. Both restrictions have been addressed through some specifically written Fortran and Python scripts.

We set five identical 2D grids, each of them including 15,537 bq (Figure 5a). The first grid was placed at the FD molecular plane, while the others were parallel and were placed above the first one. The vertical separating distance between every two sequenced layers is 0.25 Å. Thus, these grids are located at 0.00, 0.25, 0.50, 0.75 and 1.00 Å above the molecular plane.

Vector algebra has been used in some of the above scripts to allow the placing of the bq as a line (1D) of points (see Figures 5b and 5c), besides inspecting vertical cross-sections (2D; see Figures 5d and 5e). Two types of cross-sections result from setting grids perpendicular to any chosen bond. The first type comprises 8181 bq and encompasses both nuclei of the bond (Figure 5d), while the other type includes 4941 bq located at right angles to the first type (Figure 5e), equally dividing the bond. Both grid types are orthogonal to each other and their centers, that is, the origin points, absolutely match the bond midpoint.

The values of distance (spacers) among bq are adjustable. For example, 0.05 and 0.1 Å spacers were respectively applied among bq of 2D and 3D grids. Due to the variation in bond distance from one bond to another, the separating distance among bq in the 1D grids is variable. To make this point clearer, supposing any bond of FD as “A–B”, 71 bq were equally distributed along A–B as a 1D grid. The first and the last bqs, that is, bq number 1 and 71, possess the same Cartesian coordinate of nuclei A and B, respectively. Bq number 36 is located at the bond midpoint. Eventually, all the bq are evenly distanced along A–B. Thus, longer bonds make separator distances larger among bqs and vice versa. 1D calculations have helped not only probing isotropic magnetic shieldings αα(r) along bonds but also to attain NICS(0-2 Å) variation at and above the ring center (Figure 5c).

For 3D grids, the numbers of bq were 120,156, 163,800 and 107,849, which respectively evaluated the magnetic shieldings of cis, TS and trans FD.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords:** aromaticity · chemical bonding · furfuraldehyde · nucleus-independent chemical shift NICS · off-nucleus isotropic shielding

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