Briefly explore whether the compound cyclobuta[1,2:3,4]di[5]annulene possesses aromaticity

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Abstract

Studies have shown that the structure of the cyclobuta[1,2:3,4]di[5]annulene molecule is very unique, and due to its cyclic symmetry and double-bond configuration, many scholars believe that it may have aromaticity. However, there is still controversy in the academic community about whether this compound belongs to the aromatic group. Some scholars believe that it has aromaticity because its molecular plane is very flat and can satisfy Huckel's rule, while others believe that the compound does not have aromaticity because there are no cyclic coplanar π electrons on its aromatic ring. Therefore, it is important to clearly identify the aromaticity of cyclobuta[1,2:3,4]di[5]annulene for current research. In this study, theoretical and computational chemistry tools, Gaussian and Multiwfn, were used to explore the aromaticity of this compound.

Keywords: theoretical and computational chemistry, aromaticity, Gaussian, NICS, ICSS, AICD, Multiwfn

1 Preface

This study used theoretical and computational chemistry tools to explore the aromaticity of the compound cyclobuta[1,2:3,4]di[5]annulene. Among them, Gaussian is a commonly used quantum chemistry calculation software, mainly used for molecular orbital calculations, molecular dynamics simulations, and reaction mechanism studies. Multiwfn is a multifunctional computational chemistry analysis tool that can analyze molecular orbitals, molecular structures, charge distribution, and reaction mechanisms in detail. Based on these two tools, the following analyses were carried out in this study:

First, the molecular orbital diagram of the compound was calculated using Gaussian, including information such as natural orbitals, molecular orbital energy level distribution, molecular orbital corresponding orbital diagram, and natural bond orbitals. Then, the electron affinity, ionization potential, polarizability, and HOMO/LUMO energy levels of the molecular system were calculated and analyzed.

Secondly, Multiwfn was used to further verify the aromaticity. Specifically, in this study, ACID, NICS, and ICSS parameters were calculated using Multiwfn to evaluate the aromaticity of the compound. Among them, the ACID method evaluates aromaticity by calculating the electron localization function of each atom in the molecule. The NICS method evaluates aromaticity by calculating the magnetic effect of π electrons on the molecular surface. The ICSS method evaluates aromaticity by calculating the orbital divergence on the ring in the molecule.

Finally, this study used the HOMA method to evaluate the aromaticity of the compound, which evaluates aromaticity by calculating the bond length of C-C bonds on the ring. Although this method is limited for very flat molecules, the HOMA method can be used for cyclobuta[1,2:3,4]di[5]annulene, which is a very flat compound.

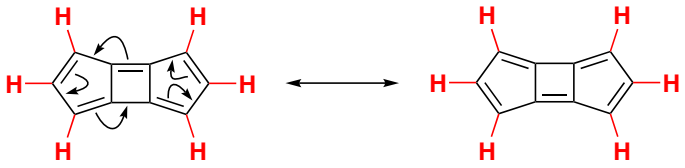

Figure 1: cyclobuta[1,2:3,4]di[5]annulene

2 Introduction to Theoretical and Computational Chemistry Tools

2.1 Gaussian and Gaussian View

Gaussian is a popular computational chemistry software that can theoretically study the electronic structure and reaction mechanism of molecules. It uses density functional theory (DFT[1]) in quantum mechanics and calculations based on Hartree-Fock[2] method to simulate the charge distribution, vibrational frequency, spectral properties, etc. of molecules. The use of Gaussian software can assist chemists in chemical structure design, drug development, and other fields.

Gaussian View is a companion program of Gaussian software, which provides a user-friendly interface for users to analyze and visualize molecular structures with convenience. It can display calculation results, such as molecular orbitals, charge density, cohesion energy, etc. Moreover, It can perform various operations such as geometric configuration optimization, energy surface scanning, ground state optimization, etc., greatly facilitating the user experience. Gaussian View also provides various output formats, such as high-definition molecular images, dynamic orbital animations, X-Y curves, etc., for users' result presentation and analysis.

This study mainly uses Gaussian 16 VX2 for calculation under the Fedora Linux system and Gaussian View 6 for visualization assistance.

2.2 Multiwfn

Multiwfn[3] is a free computational chemistry software developed by Beijing Kein Research Center for Natural Sciences that analyzes and post-processes quantum chemical calculation results. It supports the output file formats of multiple calculation programs such as Gaussian and VASP and has various analytical properties such as molecular orbitals, electron density, reactivity index, and entropy. Multiwfn is also known for its powerful graphics capabilities. Users can use it to draw various three-dimensional images, such as molecular orbitals and molecular surfaces, to intuitively understand and explain calculation results.

Multiwfn's powerful functionality comes from a combination of over 200 methods, including electronic eigenstates, molecular orbitals, topological analysis, reactivity indices, and ground state optimization, etc. Users can choose the appropriate calculation method according to their needs. Compared with other computational chemistry software, Multiwfn's biggest advantage lies in its powerful data analysis and visualization functions. It has a friendly user interface and rich documentation, making it easy for chemists with limited skills to perform analytical work.

The version used in this study is Multiwfn 3.8 dev.

2.3 AICD

AICD[4] can provide assistance in drawing magnetic induction current distribution maps. Magnetic induction current maps visualize the distribution of induced current in conductors in a magnetic field. This type of map can intuitively show the direction and intensity of current flow and is of great help in solving electromagnetic problems in conductors in a magnetic field.

AICD can use deep learning technology to automatically identify conductors and their shapes in a magnetic field, predict the distribution of magnetic induction currents inside them, and finally generate magnetic induction current maps. In addition, AICD can use image processing and computer graphics technology to visualize distribution data to help engineers and scientists better understand and analyze this data.

Therefore, AICD can assist researchers and businesses to produce faster and more accurate magnetic induction current maps and analyses in electromagnetic-related fields, improving the research efficiency and quality of magnetic induction current.

3 Methods for Measuring Aromaticity

3.1 What is Aromaticity[5]

Aromaticity is an important concept in chemistry, although its meaning is often not clear enough. It usually refers to the special chemical and physical properties possessed by compounds containing a benzene

ring or similar structures. These compounds have unique odors and tastes, as well as a certain degree of stability and solubility. The Huckle rule was the oldest indicator used to measure aromaticity, but more and more experiments have shown its significant limitations. Now, there are dozens of indicators for measuring aromaticity, and new indicators continue to emerge. These indicators reflect different aspects of aromaticity, but most rely on quantum chemical calculations. Because there is no exact and unique definition for aromaticity, the term covers an increasingly wide range of content, making it difficult to provide a simple, precise, and widely accepted definition. Aromatic substances are typically reactive and can absorb ultraviolet and visible light through the delocalization of electrons in the molecule while allowing for the production of resonance structures in the electron structure of the molecule to demonstrate stability. For most aromatic systems, they usually possess multiple characteristics simultaneously, such as balancing bond length, electron delocalization, formation of cyclic induced current under external magnetic field, higher delocalization energy, structural stability, etc. Therefore, to better describe aromaticity, it is necessary to comprehensively consider multiple aromaticity indicators based on different properties of the molecule. The following section will introduce the indicators used to measure aromaticity in this article.

3.2 NICS(0) and NICS(1)_zz

NICS[6] stands for nucleus-independent chemical shift and is an index used to measure aromaticity. It was initially defined as the negative value of the isotropic chemical shieldings at the geometric center of heavy atoms in the ring. The NICS index was proposed to supplement the shortcomings of the Hückel rule and its variants.

The NICS index is derived from chemical shift (CS) computed from computational simulations, where the nucleus-independent chemical shift (NICS) index can be obtained by introducing a ”test” nucleus at a specific location. NICS can be used to calculate aromaticity in compounds containing one or more aromatic rings and determine the differences in aromaticity among different rings.

For an aromatic system, the isotropic chemical shieldings are generally positive, and NICS values are negative. The following code calculates the NICS (0) of cyclobuta, with the geometry-optimized structure of the molecule:

```
# nmr=giao b3lyp/6-31+g(d)

cyclobuta

0 1
C                  -2.02780100    1.19593100    0.00000100
C                  -0.71262400    0.75091200    0.00000000
C                  -0.71274400   -0.75106900   -0.00000200
C                  -2.02777100   -1.19599300    0.00000200
C                  -2.80679600    0.00019300    0.00000000
```

```
H                -2.42162200    2.20431100    0.00000200
H                -2.42134300   -2.20448100    0.00000400
H                -3.89445200    0.00041300    0.00000200
C                 0.71258100    0.75076100   -0.00000100
C                 2.02785900    1.19592300   -0.00000300
C                 2.80694000    0.00009700    0.00000700
C                 2.02775700   -1.19590500   -0.00000200
C                 0.71264600   -0.75094200   -0.00000600
H                 2.42139700    2.20440000   -0.00000500
H                 3.89458100    0.00035200    0.00001200
H                 2.42115400   -2.20444500   -0.00000100
Bq               -1.65754720   -0.00000520    0.00000020
Bq               -0.00003525   -0.00008450   -0.00000225
Bq                1.65755660   -0.00001320   -0.00000100
```

The NICS value of the edge ring is -9.0244, and that of the central ring is -2.1278. Since both NICS values are negative, it indicates that the ring structures in the molecule exhibit aromaticity. The more negative NICS value of the edge ring indicates stronger aromaticity. It should be noted that the previously calculated NICS values were all NICS(0), which has limitations. Therefore, it is recommended to use NICS(1)_zz[7] for better measurement of aromaticity. The detailed method for calculating NICS(1)_zz can be found in Sobereva's article[8]. The NICS(1)_zz calculation of the molecule is still performed using the b3lyp/6-31+g(d). The following is the calculation code.

```
# nmr=giao b3lyp/6-31+g(d)

cyclobuta

0 1
C                -2.02780100    1.19593100    0.00000100
C                -0.71262400    0.75091200    0.00000000
C                -0.71274400   -0.75106900   -0.00000200
C                -2.02777100   -1.19599300    0.00000200
C                -2.80679600    0.00019300    0.00000000
H                -2.42162200    2.20431100    0.00000200
H                -2.42134300   -2.20448100    0.00000400
H                -3.89445200    0.00041300    0.00000200
C                 0.71258100    0.75076100   -0.00000100
C                 2.02785900    1.19592300   -0.00000300
C                 2.80694000    0.00009700    0.00000700
C                 2.02775700   -1.19590500   -0.00000200
C                 0.71264600   -0.75094200   -0.00000600
H                 2.42139700    2.20440000   -0.00000500
H                 3.89458100    0.00035200    0.00001200
```

```
H                  2.42115400    -2.20444500    -0.00000100
Bq                 -1.6575461305    -0.0000050591     1.0000003600
```

To save time, only the NICS_zz value of the edge ring was calculated, and the result is shown below:

```
The magnetic shielding tensor you inputted is:
XX=   -1.624700   YX=   -0.004600   ZX=    0.868100
XY=   -0.003400   YY=    5.055000   ZY=    0.001000
XZ=   -1.899000   YZ=   -0.000700   ZZ=   27.578900
The shielding value normal to the plane is       27.5788989180
The NICS_ZZ value is thus      -27.5788989180
```

After computation, it was determined that the NICS(1)_zz of the edge ring in the molecule is -27.5788989180, providing further evidence of its strong aromaticity.

3.3 AICD

Apart from NICS values, AICD is also an important indicator for measuring aromaticity. AICD (Anisotropy of the Induced Current Density) represents the degree to which the local charge density in a molecule deviates from the plane along different directions[9]. In aromatic compounds, their AICD values are lower because the aromatic current sinks down along the center of the ring structure, leading to a decrease in aromatic local charge density.

$$\Delta T_S^{(1)^2} = \frac{1}{3}\left[(t_{xx}-t_{yy})^2+(t_{yy}-t_{zz})^2+(t_{zz}-t_{xx})^2\right]$$
$$+\frac{1}{2}\left[(t_{xy}+t_{yx})^2+(t_{xz}+t_{zx})^2+(t_{yz}+t_{zy})^2\right]$$

The AICD program is designed to draw AICD contour and induced current vectors, and its installation process is well-documented in Sobereva's article[10]. The code listed below is added to the optimized molecule file (gjf):

```
# nmr=csgt b3lyp/6-31+g(d) IOp(10/93=1)

cyclobuta

0 1
C                  -2.02780100    1.19593100    0.00000100
C                  -0.71262400    0.75091200    0.00000000
C                  -0.71274400   -0.75106900   -0.00000200
C                  -2.02777100   -1.19599300    0.00000200
C                  -2.80679600    0.00019300    0.00000000
H                  -2.42162200    2.20431100    0.00000200
H                  -2.42134300   -2.20448100    0.00000400
```

```
H                    -3.89445200     0.00041300     0.00000200
C                     0.71258100     0.75076100    -0.00000100
C                     2.02785900     1.19592300    -0.00000300
C                     2.80694000     0.00009700     0.00000700
C                     2.02775700    -1.19590500    -0.00000200
C                     0.71264600    -0.75094200    -0.00000600
H                     2.42139700     2.20440000    -0.00000500
H                     3.89458100     0.00035200     0.00001200
H                     2.42115400    -2.20444500    -0.00000100

test.txt
```

The command below is used to execute the Gaussian 16 program with the above file and to generate cyclobuta.out and test.txt files:

```
g16 <cyclobuta.gjf |tee cyclobuta.out
```

As the resulting molecule is nearly perpendicular to the z-axis, the external magnetic field vector should be 0 0 1. In the terminal, type:

```
AICD -m 4 -b 0 0 1 -pov cyclobuta.out
```

The Povray renderer can be used to render the generated RenderMich.pov file, and the resulting image clearly shows the existence of ring currents in cyclobuta[1,2:3,4]di[5]annulene.

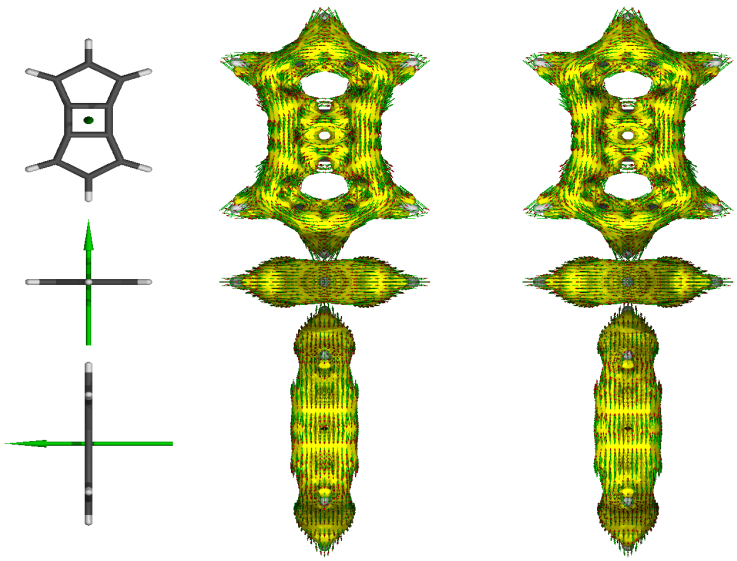

Figure 2: The anti-magnetic ring current diagram of cyclobuta[1,2:3,4]di[5]annulene

In addition, Sobereva[11] reported the ability to extract the contributions of each orbital in the molecule

in their study. In order to obtain all the π orbitals in the molecule, the Multiwfn program was used to search for all the numbers of π molecular orbitals (π MO numbers)[12]. The following code was obtained by modifying the above mentioned code.

```
# nmr=csgt b3lyp/6-31+g(d) IOp(10/93=2)

cyclobuta

atomic coordinates were omitted and remain unchanged from the previous section

test.txt

24
29
31
32
33
```

Following the aforementioned steps, the resulting plot is depicted in the subsequent figure:

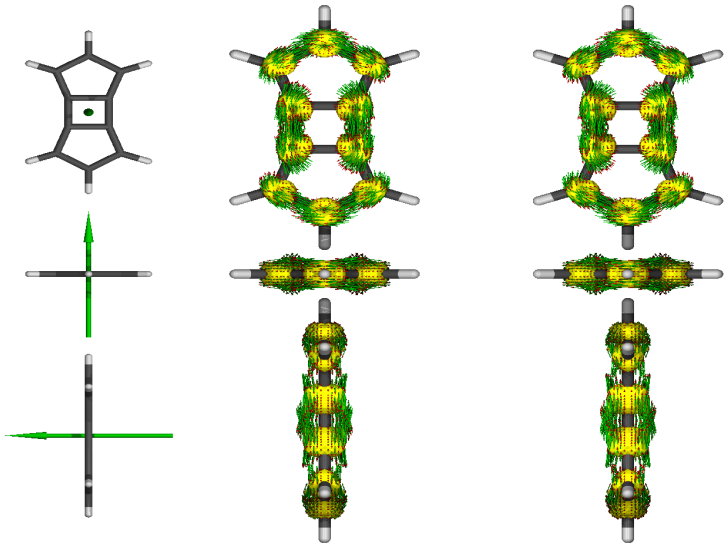

Figure 3: The anti-magnetic ring current diagram of cyclobuta[1,2:3,4]di[5]annulene for π orbitals

By comparing the anti-magnetic ring current diagram (Figure 2 and Figure 3) constructed using only π orbitals and all molecular orbitals, we observed differences in the results. The ring current map generated from only π orbitals exhibited distinct breaks in the ring, while the full ring current map clearly showed a ring current. Therefore, it is not ideal to use AICD to determine the aromaticity of cyclobuta[1,2:3,4]di[5]annulene.

3.4 HOMA

The HOMA (Harmonic oscillator measure of aromaticity) index is a measure of a molecule's aromaticity[13]. It is based on calculating the degree of aromaticity of carbon-carbon bonds in a molecule to determine its aromaticity. The index measures the degree of aromaticity by the extent to which the π electrons deviate from the equilibrium position of a simple dipole moment when forming the ring structure. HOMA values range from 0 to 1, where 0 represents the complete loss of aromaticity and 1 represents complete aromaticity. This index can be used to compare the relative aromaticity of different molecules, as standard HOMA values provide quantitative information. The expression is given as follows:

$$\mathrm{HOMA} = 1 - \sum \frac{\alpha_{i,j}}{N} \left(R_{\mathrm{Ref}-R_{i,j}}\right)^2$$

Here, according to the article by Sobereva[14] (section 4.1), Multiwfn was used to calculate the HOMA values of the molecule, and the results are shown below:

```
1,2,3,4,5

Atom pair          Contribution  Bond length(Angstrom)
1(C )  --    2(C ):       -0.000009        1.388429
2(C )  --    3(C ):       -0.669589        1.501981
3(C )  --    4(C ):       -0.000003        1.388256
4(C )  --    5(C ):       -0.080394        1.427495
5(C )  --    1(C ):       -0.078803        1.427102
HOMA value is    0.171200

2,3,13,9

Atom pair          Contribution  Bond length(Angstrom)
2(C )  --    3(C ):       -0.836986        1.501981
3(C )  --   13(C ):       -0.090067        1.425390
13(C )  --    9(C ):       -0.832911        1.501703
9(C )  --    2(C ):       -0.089177        1.425205
HOMA value is   -0.849141

9,10,11,12,13

Atom pair          Contribution  Bond length(Angstrom)
9(C )  --   10(C ):       -0.000017        1.388570
10(C )  --   11(C ):       -0.079291        1.427223
11(C )  --   12(C ):       -0.080117        1.427427
12(C )  --   13(C ):       -0.000006        1.388347
13(C )  --    9(C ):       -0.666329        1.501703
HOMA value is    0.174241
```

The HOMA values of the outer rings of cyclobuta[1,2:3,4]di[5]annulene are almost 0, but still slightly above 0, while the inner ring has a negative HOMA value, indicating antiaromaticity. This indicates that the inner ring is antiaromatic. Therefore, it suggests that the outer rings have weak molecular aromaticity, but still exhibit some aromatic properties, while the inner ring is completely non-aromatic.

3.5 ELF-sigma/pi and LOL-sigma/pi

ELF (The electron localization function) is an indicator used to evaluate electron localization in a molecule. ELF-σ and ELF-π are used to study σ and π aromaticity[15].

As the isovalue increases, the space (called domains) within the ELF isovalue gradually decreases. If multiple local maxima are contained in a single ELF isovalue surface, the domain can be decomposed into multiple isolated irreducible domains, each containing only one ELF maximum. Generally, molecules with ELF-π greater than 0.7 are considered to be π aromatic, while those with values between 0.11-0.35 are considered to be π antiaromatic. For organic molecules, the average ELF-π and ELF-σ values greater than 0.7 indicate overall aromaticity, and values less than 0.55 indicate overall antiaromaticity[16].

We can use Multiwfn to calculate the ELF-σ and ELF-π isovalue surface maps of the molecule cyclobuta[1,2:3,4]di[5]annulene at different isovalue levels[17]. The figure is shown below:

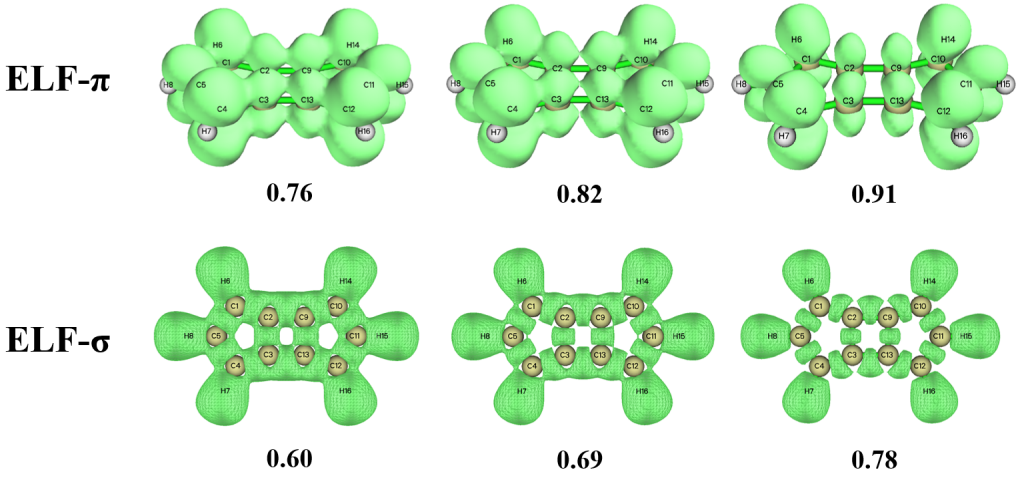

Figure 4: The ELF-σ/π of cyclobuta[1,2:3,4]di[5]annulene

LOL (Localized Orbital Locator) is a method for localizing the central atoms and chemical bonds in a molecule[18]. It utilizes the results of quantum chemical calculations to generate a visualization tool, which shows the spatial distribution and location of the molecular orbitals. This helps us to better understand the electronic structure and properties of chemical bonds in a molecule.

The LOL-π fill map at 1.2 Bohr above the plane of the molecule was generated using the method

described by the article of sobereva[19], with Multiwfn.

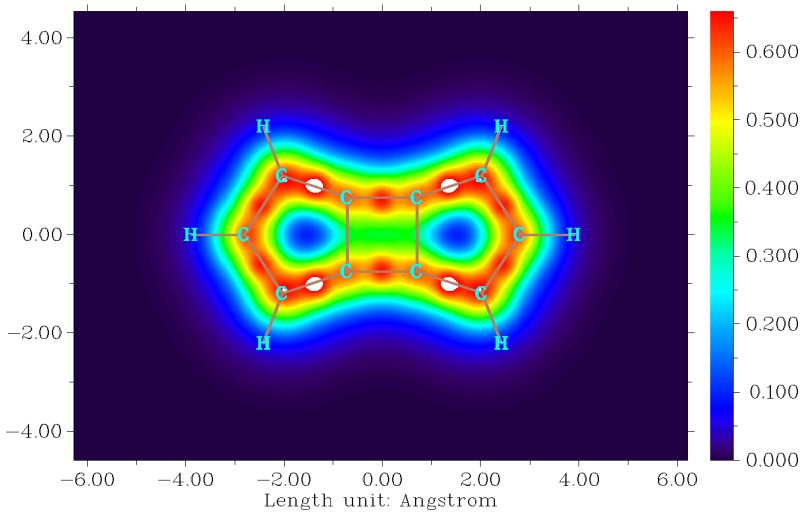

Figure 5: The LOL-π fill map at 1.2 Bohr of cyclobuta[1,2:3,4]di[5]annulene

Both ELF and LOL diagrams show the overall aromaticity of the cyclobuta[1,2:3,4]di[5]annulene molecule. However, there are four white spots in the LOL diagram, and the specific reason is not clear. This may be due to the small value of HOMA.

3.6 ICSS

ICSS (Iso-Chemical Shielding Surfaces) is a tool for studying steric and nonplanarity effects[20]. It is defined by following the isosurfaces of equal chemical shielding along the chemical bond. This approach is more intuitive and displays richer information compared to the traditional method of calculating NICS values at the ring center.

Similarly, sobereva introduced the method of using Multiwfn to calculate ICSS_zz in his article[21][22]. It should be noted that the symbols for ICSS and NICS are opposite. NICS takes the negative value of magnetic shielding, which means that the more negative the NICS value is, the stronger the shielding effect of the external magnetic field is on that point. The more positive the NICS value, the stronger the non-magnetic shielding effect at that location. On the other hand, ICSS directly displays the magnetic shielding value without the need to take the negative value.

Similar to NICS, ICSS_zz is more accurate than ICSS, as shown in the ICSS_zz contour map with the contour value of 2.0. In the plot, the green contour represents the region with magnetic shielding of 2 ppm, while the blue contour represents the deshielding region with a shielding value of -2 ppm or a deshielding value of 2 ppm.

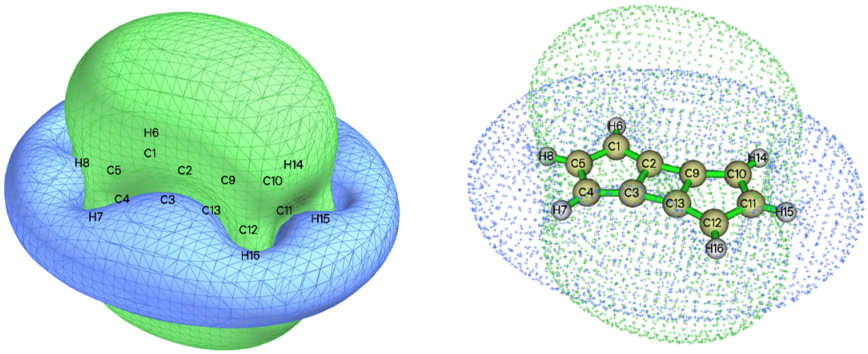

Figure 6: The ICSS_zz isosurface map of cyclobuta[1,2:3,4]di[5]annulene

From the ICSS_zz contour map of cyclobuta[1,2:3,4]di[5]annulene, the green region is located inside the ring, indicating a shielding effect. The blue region around it further indicates that there is a region outside the ring for deshielding. Therefore, the molecule has ring current, indicating aromaticity of the molecule.

4 Summary

The present study employs theoretical and computational chemistry to analyze the aromatic properties of cyclobuta[1,2:3,4]di[5]annulene.

The LOL-π fill map generated using the method described by Sobereva[19] with Multiwfn and the ELF diagrams indicate that the molecule has some degree of aromaticity. ICSS_zz was calculated using Multiwfn, as introduced in Sobereva's article[21][22]. ICSS_zz isosurface map results show that the molecule has a ring current, indicating its aromaticity.

This study has its limitations, and further research and analysis are needed using other influencing factors to gain a more comprehensive understanding of the aromatic properties of this compound.

We sincerely thank Sobereva, the president of the computational chemistry society, for their valuable blog posts and guidance. Moreover, the computational methods and theoretical foundations used in this study have their limitations, and we welcome any corrections and guidance.

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