Structure, Stability and Aromaticity of Linear Acenes

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Abstract

It is contribute to provide theoretical reference for the synthesis of more aromatic compounds in experiment for finding a method to quantitatively determine the aromaticity. In this study, Density Functional Theory (B3LYP/6-311+g (d,p)) method were used to optimize the geometry of linear acenes. The Ring Stretching Vibration Raman Spectral Frequency (RSVRSF), nuclear independent chemical shift (NICS), aromatization stabilization energy (ASE), bond length averaging energy (EBLE), degree of aromaticity (DOA), delocalization energy (DE) and delocalization energy (DE/per C-C double bond) of linear acenes were calculated via Gaussian 09 package. The results show that there is a significant correlation between the NICS values, the values of DOA and RSVRSF. Meanwhile, the values of DE are also highly correlated with the values of DOA, NICS and RSVRSF. Therefore, RSVRSF, DOA and DE can be used as new criteria to judge the aromaticity of the central ring of linear acenes. It is theoretically predicted that the aromaticity of linear acenes can be measured by measuring the RSVRSF of the molecule.

Introduction

Linear acenes compounds are one kind of Polyacene compounds. Their molecular formulas can be expressed by the general formula of CₙH₂ₙ₊₄. Because linear acenes are compounds consisting of benzene rings, each six-membered ring has six π electrons, so each ring satisfies the Hückel (4n+2) π electronic rule and is aromatic. At present, the study of the total aromaticity and local aromaticity of linear acenes compounds has attracted the interest of scientists [1]. As for the aromaticity of linear acenes compounds, the most interesting topic concerns the trend towards global and local aromaticity, that is, does the central ring exhibit stronger aromaticity than the peripheral ring? Researchers used magnetic criterion (NICS), bond length averaging energy (EBLE), degree of aromaticity (DOA), delocalization energy (DE) and the Shannon entropy concept to study aromaticity of linear acenes [2-6]. However, it is found that these criteria are based on theoretical calculation. Up to this time, there is no accurate method to quantitatively measure the aromaticity of the central ring of linear acenes. They evaluated the aromaticity index as a mono-dimensional extensive quantity of linear acene. Either just consider the energy factor or in the only aspect of the magnetic variation factor. There has not been an index that comprehensively considers the strength properties of two or more factors to determine the size of linear acene aromaticity.

In previous, our research group proposed a new criterion for determining aromaticity the Aᵣ/ₐᵣ. Ring Stretching Vibration Raman Spectral Frequency (RSVRSF). And they investigated the correlation between the NICS and RSVRSF (Aᵣ/ₐᵣ) of the high-symmetric cyclic conjugated compound and the semi-sandwich in theory. It is found that the value of RSVRSF (Aᵣ/ₐᵣ) of the target aromatic compound is significantly correlated with the aromatic degree of the molecule (NICS). It is predicted that the value of the RSVRSF (Aᵣ/ₐᵣ) can be used as the aromatic probe of the aromatic compound. That is the value of the RSVRSF can be used as an experimental criterion for determining the aromatic degree. So the experimental determination of the aromatic degree can be achieved by determination of the Ring Stretching Vibration Raman Spectral Frequency for the aromatic target molecules [7-9]. Recently, a new aromaticity index is proposed, which takes into account both energy and magnetic factors. It is found that the aromaticity of highly symmetric cyclic conjugated compounds can be predicted by calculating the Degree of Aromaticity (DOA) [10]. Whether these two new criteria can be applied to determine the aromaticity of linear acenes will be the primary issue for our further study.

Based on the above problems, we used quantum chemical methods to study the aromaticity, Raman spectrum frequency, the Bond Length Equalization (BLE) process and delocalization energy of linear acenes. A comprehensive aromaticity index criterion considering bond length equalization, ring radius size, bond energy change and stabilization energy change was found, and the ring stretching Raman spectra of these molecules were explored. The correlation between the frequency and the aromaticity of the substance was studied. A new method for determining the aromaticity of the substance by experimental means was found in theory.

Experiment and calculation methods

Experimental Methods and Techniques

Experimental instrument: RENISHAW in Via Microscope Raman.

Experimental reagents: benzene (≥99.9%, GC), naphthalene (≥99.5%, GC), anthracene (≥99.5%, GC).
Experimental conditions and methods: Benzene (laser wavelength 532 nm, scanning range 100-4000cm-1, exposure time 1s, laser power 10% (3.0mW), scanning 30 times); Naphthalene, Anthracene (laser wavelength 532 nm, scanning range 100-4000cm-1, exposure time 1s, laser power 10% (3.0mW), scanning 20 times)

Theoretical calculation methods

The geometric optimization of $C_{4n^2}H_{2n+4}$ molecule was carried out by Gaussian09 quantum chemical calculation program, density functional theory (DFT), B3LYP calculation method and 6-311G (d, p) basis group. The stable structure of $C_{4n^2}H_{2n+4}$ molecule was calculated and the Ring Stretching Vibration Raman Spectral Frequency (RSVRSF), the stability (DE/per) of target molecules, aromatic stabilization energy (ASE), Bond Length Equalization energy (EBLE), DOA and C-C symmetric type of A1g/A1 molecule were calculated. The DE/per of the double bond is used to calculate the nuclear independent chemical shifts (NICS) of the target molecule by the B3LYP-GIAO method. The correlation and correlation coefficients between the experimental criteria (RSVRSF), theoretical criteria (NICS, DOA) and stability (DE/per) of aromatic molecules were studied by using Origin 8.0. Gauss View 5.0 was used to draw target molecular structure and characteristic molecular orbital map. Origin 8.0 was used to plot the correlation curves between NICS, RSVRSF, DOA and other parameters of target molecule.

Results and discussion

Geometric and electronic structure analysis

The point group of linear acenes is the stable structure of D2h (the point group of benzene removal is D6h). The target molecule has no imaginary frequency and can exist stably. Fig. 1 is the optimized molecular structure of benzene and naphthalene. The large π bonds of benzene are evenly distributed on six carbon atoms, so the bond lengths and bond energies of each C-C bond in benzene molecule are equal. The structure of naphthalene and anthracene is similar to that of benzene. The molecular formula of naphthalene (in Fig. 1) is $C_{10}H_8$. However, the structures of naphthalene and benzene are not identical. In addition to overlapping each other, the π orbitals of the two common carbons in the naphthalene molecule overlap with the $p$ orbitals of the other two adjacent carbons respectively. Therefore, the closed large π bond electron cloud is not uniformly distributed on the naphthalene ring, resulting in the incomplete equivalence of the length of the C-C bond. Anthracene is also a planar molecule. Due to the cohesion of two carbon atoms between the rings, the overlap degree of each $2p$ orbital is not exactly the same, so the C-C bond length is not completely equal. Fig. 1 shows the C-C average bond lengths of benzene and naphthalene as central rings of odd and even linear acenes, respectively. Table 2 shows the C-C average bond lengths of central rings of odd and even linear acenes. It shows that the average bond length of C-C bond in central ring increases with the increase of benzene ring, but the increase of C-C bond length is very small (0.002-0.03 Å). The reason for the change of bond length is analyzed. Compared with benzene, the bonding atoms on the center ring of odd linear acenes are all carbon atoms. Besides bonding on the center ring, the carbon atoms on the ring also bond with the atoms outside the center ring. Two carbon atoms are bonded with hydrogen atoms, and the other four carbon atoms are bonded with carbon atoms. The number of electronic layers of carbon atoms is more than that of hydrogen atoms, which leads to the number of electronic layers between C-C. The distance between nuclei is larger than that between C-H, that is, the bond length of C-C bond is longer than that of C-H bond. Due to the carbon atoms in the center ring of odd linear acenes interact with the carbon and hydrogen atoms outside the ring, the C-C bond lengths in the center ring are different, which results in the difference of the average bond lengths of the C-C bond in the center ring. The C-C bond length changes slightly, mainly because the bonding atoms of C-C bond are all carbon atoms, and the nucleus spacing changes slightly. Hence, the interaction force of C-C bond of central ring of odd linear acenes basically remains unchanged. Unlike odd linear acenes, even linear acenes use benzene as their cardinal ring, while even linear acenes use naphthalene as their cardinal ring, that is, naphthalene as the central ring of even linear acenes. After optimization, the average C-C bond length of the central ring increases gradually, but the increase range of the C-C bond length is very small (0.002-0.002 Å). From the increase range of the bond length, it can be seen that the interaction force of the C-C bond of central ring of even linear acenes is basically unchanged.

![Figure 1: The geometric structure and C-C bond length of cardinal ring of linear acenes (a) (benzene-CH$_2$H$_8$) (b) (naphthalene-CH$_4$H$_8$)](image)

The electronic structure of linear acenes was further analyzed. The number of π electrons of linear acenes satisfies the Hückel (4n+2) π electronic rule. The occupied orbital of linear acenes after structural optimization was analyzed. It was found that linear acenes have both π aromaticity and σ aromaticity. Characteristic molecular orbitals of linear acenes are shown in Figure 2. Among them, HOMO-4 of C₆H₆, HOMO-7 of C₁₀H₈, HOMO-11 of C₁₄H₁₀, HOMO-14 of tetra biphenyl (C₁₈H₁₂), HOMO-18 of pent biphenyl (C₂₂H₁₄) and HOMO-21 of hex biphenyl (C₂₆H₁₆) are all conjugated large π bonds formed by the pz orbitals of carbon atoms side by side, which induce the formation of π electron circulation, showing π aromaticity. At the same time, σ electrons generate σ orbitals of HOMO-9 of C₆H₆, HOMO-23 of C₁₀H₈, HOMO-32 of C₁₄H₁₀, HOMO-41 of C₁₈H₁₂, HOMO-50 of C₂₂H₁₄ and HOMO-59 of C₂₆H₁₆, which induce σ-ring current, i.e. σ aromaticity. σ aromaticity is formed by the hybridization of carbon (s, px, py).

There are also cyclic π and σ orbitals for the following molecules: C₃₀H₁₈ to C₄₂H₂₄. The characteristic molecular orbitals are not shown in Fig. 2. The aromaticity of the target molecule is related to its conjugation (i.e. cyclic conjugated π and σ bonds), which determines the interaction force between adjacent atoms in the aromatic molecule. The magnitude of the conjugation force can be determined by the force constant of the target molecule. The spectrum of the target molecule is RSVRSF (A1g). It is concluded that the values of RSVRSF must be related to its aromaticity.

Figure 2: Partial characteristic molecular orbital maps of linear acenes molecules

Bond length equalization process and aromaticity in linear acenes

Traditional chemistry books still use regular hexagons when they write Kekulé type of benzene, but only double bonds are added to the ring, which cannot distinguish Kekulé type from large offshore π bond accurately. In fact, the single-double bond alternating Kekulé formula belongs to the D₃h molecular point group, while the bond length equalization of benzene belongs to the D₆h molecular point group. In the bond length equalization process, single bond shortens, double bond lengthens, molecular symmetry increases, electron delocalization, chemical properties become more stable, that is, aromaticity increases. Fig. 3 shows the bond length equalization process of benzene.

From the bond length equalization process of benzene in Fig. 3, we can see that the structure on the left side is θ₁>θ₂ and BL₁>BL₂, while the structure on the right side shows the structure with the same ring bond length, that is, θ₁=θ₂ and BL₁=BL₂. From the left structure to the right structure is bond length equalization process. In this process, the bond angle θ₁ corresponding to a single bond decreases gradually, and the bond angle θ₂ corresponding to a double bond increases gradually. Finally, when θ₁=θ₂, the ring bond length is equal, that is, BL₁=BL₂. In the left structure (in Fig. 3), single-double bond alternating structure is determined by the determination of angle of the central ring. The angle of the central ring is adjusted to make the ratio of double bond length to single bond length of the molecule by 0.8683, i.e. BL₁/BL₂ = 0.8683. The determination of the bond angles (θ₁, θ₂) and bond lengths (BL₁, BL₂) after adjusting the six-membered ring is shown in Fig. 4. According to the radius of Fig. 4, the relationship between the center angle and the chord length has an equation:
Figure 3: An illustration of C6C6 in the process of Bond Length Equalization (BLE)

Figure 4: An illustration to display the relationship between ring radius, ring angle and bond length

\[\begin{align*}
3\theta_1 + 3\theta_2 &= 360^\circ \\
BL_1 &= 2r \sin(\theta_1 / 2) \\
BL_2 &= 2r \sin(\theta_2 / 2) \\
BL_1 / BL_2 &= 0.8683
\end{align*}\]

It can be found that \(\theta_1 = 64.7^\circ\), \(\theta_2 = 55.3^\circ\), \(BL_1 = 1.4917\), \(BL_2 = 1.2953\).

The calculation of Bond Length Equalization energy (EBLE) is the difference between the single point energies of the two structures of the same molecule (the difference between the energies of the two structures of C6H6 in Fig.3). In Fig. 3, the structure with the same ring bond length on the right is optimized by the quantum chemistry software Gauss09, and the structure on the left is obtained by adjusting the center angle of the ring on the right. Keeping the radius of the ring unchanged, the central angles of the molecule \(\theta_1\) and \(\theta_2\) are adjusted so that the molecule can form a single-double bond alternating structure. Because there are more than one cycles of linear acenes (except benzene), and the bond length equalization energy of each ring is different, that is, the energy reduced by electron delocalization is different. Hence, the bond length equalization energy of linear acenes can be divided into the whole bond length equalization energy and the bond length equalization energy of one of the rings. As shown in Fig. 5 (a) and (b), they are single-double bond alternating structures of central rings of odd and even linear acenes. The bond lengths of other rings are consistent except that the central ring is single-double bond alternating structure. The single-point energy is calculated by using Gaussian09. Fig. 5 (c) is whole single-double bond alternating structure of anthracene. Fig. 5 (d) is a single-double bond alternating structure of one of the ring of even linear acenes central ring. The other environmental bond-holding length of the central ring is the same. The bond length equalization energy is the difference between the optimized energy of linear acenes and the adjusted energy of single-double bond structure of linear acenes. For central ring of anthracene, the bond length equalization energy of the whole ring and central ring are listed in formulas (3-2-1) and (3-2-2), respectively. The formulas (3-3-3) and (3-3-4) are the bond length equalization energy of tetra benzobenzene central ring and naphthalene one ring, respectively. The bond length equalization of other linear acenes central rings and whole rings are similar to those of anthracene and napththalene.
Structure, Stability and Aromaticity of Linear Acenes

Figure 5: The central ring single-double bond alternating structure (a) (b), the whole single-double bond alternating structure (c) of a part of linear acenes and one of the naphthalene rings single-double bond alternating structure (d).

EBLE = Energy of linear acenes - linear acenes Energy after structural adjustment.

Anthracene: $E_{ble} (Central \ ring) = E_{C_{14}H_{10}} - E_c$ (3-2-1)
$E_{ble} (Whole) = E_{C_{14}H_{10}} - E_t$ (3-2-2)

Naphthacene: $E_{ble} (Central \ ring) = E_{C_{10}H_8} - E_b$ (3-2-3)

Naphthalene (One of the ring): $E_{ble} = E_{C_{10}H_8} - E_d$ (3-2-4)

Aromatic stabilization energy (ASE), i.e. Delocalized Bond Energy (EDBE), refers to the additional stabilization energy obtained by aromaticity, and also refers to the total bond energy of ring atoms. This energy can reflect the reduced energy proportion due to electron delocalization. For the optimized target molecule, adjust the radius of the optimized ring molecule, increase the radius of the ring until there is no interaction between adjacent ring-forming atoms. Then calculate the single point energy, and the delocalized bond energy is the difference between the two energies. In the calculation, the single point energy of the optimized molecule and the sum of the fragment energy of the molecule can also be calculated separately, and the difference between the two can also be used to calculate the delocalized bond energy.

Fig. 6 shows that benzene with average bond length is divided into six C-H structural monomers, and naphthalene is divided into eight C-H structural monomers and two carbon atoms. There are two sp2 single electrons and one unhybridized p electron in each C-H structure. Optimize and calculate the energy of benzene and naphthalene. There are three single electrons in the C-H monomer, so the spin multiplicity is four, there are two single electrons in the carbon atom and the spin multiplicity is three. The energy of C-H monomer and carbon atom is calculated. EDBE of benzene and naphthalene could be generalized according to the equation below:

Benzene ($C_6H_6$): $ASE = EDBE = 6E_{C\cdot H} - E_{C_6H_6}$

Naphthalene ($C_{10}H_8$): $ASE = EDBE = 8E_{C\cdot H} + EC - E_{C_{10}H_8}$

The calculation method of the whole EDBE of tribenzodecabenzo series molecule is similar to that of naphthalene molecule. The whole EDBE of naphthalene molecule is calculated according to the above method. But for one of the six-membered rings of $C_{10}H_8$, EDBE cannot be used in this method, because when the two benzene rings of $C_{10}H_8$ share two carbon atoms, the bond energy of another benzene ring is involved, so it is not possible to calculate the overall EDBE of $C_{10}H_8$. Fig. 7 is a fragment that is disassembled by calculating the EDBE of one of the six-membered rings in naphthalene.

Disassembling fragments formula (1): calculating the bond energy of the three bonds connecting two fragments. Both fragments have six single electrons, a charge of 0 and a spin multiplicity of 7.

$EDBE (1) = E_1 + E_2 - EC_{10}H_8$

Disassembling fragment formula (2): calculating the bond energy of two bonds connecting two fragments. The bond energy of the two bonds is equal to that of the two double bonds of the C-H bond in the dismantling fragment formula (1). Both fragments have four single electrons, zero charge and 5 spin multiplicity.
Figure 6: Cutting optimized molecule into fragments, keeping bond length of C-H

Figure 7: Calculating the delocalized bond energy of one of the six-membered ring molecules by splitting them into fragments in naphthalene (purple atom is virtual atom X)

Disassembling fragments formula (3): calculating the bond energy of five bonds connecting five fragments. The first four fragments have three single electrons, with charge 0, spin multiplicity 4, and the last two single electrons, with charge 0 and spin multiplicity 3.

EDBE (3) = 2E3 + 2E4 + 2E7 - E\text{C}\text{10H8}

From the formula (1), (2), (3) of the debris disassembled in Fig. 7, we can get below the delocalized bond energy of one of the rings in naphthalene.

EDBE = E\text{DBE}(1) - E\text{DBE}(2) + E\text{DBE}(3)

EDBE (1) is the delocalized bond energy of dismantling fragments (1). EDBE (2) and EDBE (3) represent the delocalized bond energy of dismantling fragments (2) and (3), respectively. The disassembly of central rings of even and odd linear acenes is shown in Fig. 8 (taking anthracene and naphthacene as examples).
Figure 8: Fragments disassembled by calculating the delocalized bond energy of central rings of anthracene and naphthacene (Calculating bond energy of red bond by dismantling red bond) (1) (2) (3) (4) (5) (6) represents the energy of the delocalized bond energy for the dismantling red bonds, respectively.

From (1), (2), (3), the delocalized bond energy of anthracene central ring can be obtained in Fig 8. The delocalized bond energy of anthracene central rings is as follows:

$$E_{DBE} = E_{DBE(1)} - E_{DBE(2)} + E_{DBE(3)}$$

From (4), (5), (6) of the tetrabenzol debris in Fig 8, the delocalized bond energy of the central ring of tetrabenzol can be obtained. Its delocalized bond energy is:

$$E_{DBE} = E_{DBE(4)} - E_{DBE(5)} + E_{DBE(6)}$$

According to the bond length equalization process and the analysis of bond energy of linear acenes, the Degree of aromaticity (DOA) was designed. The physical quantities of strength properties of two dimensions of geometric factor and energy factor were comprehensively considered in the aromaticity index. The formula of the new aromaticity index DOA was put forward as follows:

$$DOA = \frac{EBLE}{EDBE \cdot r^2}$$

EBLE represents the bond length equalization energy. EDBE is the delocalized bond energy. \( r \) is the ring radius. The designed aromaticity index DOA reflects the proportion of energy reduced by aromaticity to total bond energy, and both EBLE and EDBE are affected by the ring radius. In order to eliminate this interference, \( r^2 \) is introduced into the denominator of DOA formula. Some rings have different radius, so we take the average radius here. The radius of the whole linear acenes is taken as the average of the radius of all six-membered rings in the target molecule. The EBLE, EDBE and DOA values of the central ring of linear acenes are listed in Table 1.

From Table 1, we can see that the average bond length of the central ring is longer than the average bond length of the whole molecule, but the increasing of the C-C bond length is very small. It can be concluded that the interaction force between the C-C bond of the central ring and the C-C bond of the whole molecule is basically unchanged. With the increase of benzene rings, the delocalized bond energy of the central ring decreases and the BLE energy increases. In addition, the BLE energy of the central
Aromaticity and Raman Spectrum Frequency

On the basis of geometric optimization, the RSVRSF value of target molecule is calculated by the same basis set method, and the NICS value inside and outside the ring plane is calculated by NMR-GIAO method. The calculation results are shown in Table 2. For molecules with D6h point group, the ring-stretching vibration is obvious. Fig 9(a) is the ring stretching vibration of benzene, and the RSVRSF value is 1011.5 cm$^{-1}$. For the molecules whose point group is D2h odd linear acenes, for example, anthracene does not exhibit the ring-stretching vibration mode as in Annex 1 (see Annex 1 in Appendix), but the calculation results show that the central ring exhibits the ring-stretching vibration like benzene. Fig 9 (b) shows the ring-stretching vibration of the anthracene central ring, and the ring-stretching vibration is similar to that of benzene. The vibration mode is A1-symmetric, and the ring stretching vibration raman spectroscopy frequency corresponding to anthracene central ring is 1287.8 cm$^{-1}$. For naphthalene, there is no ring stretching vibration mode as in Annex 2 (Annex 2 in Appendix), which is simulated by using a geometric sketchpad. Because the central of the rings is on the C-C bond, but the calculation results of the left and right two rings of the C-C double bond at the central of the shared ring show no ring stretching vibration. If naphthalene is regarded as the cardinal ring of even linear acenes, the middle two rings are the central ring of even linear acenes type. Although the even linear acenes central ring does not exhibit the ring stretching vibration mode as shown in the Annex2, the calculation results show that there is a vibration mode similar to annex 2 (Annex 2 in Appendix), and the vibration mode is A1 vibration mode. As is shown in Fig 9 (c), the corresponding RSVRSF value is 771.9 cm$^{-1}$. In Annex 3 in Appendix, the ring stretching vibration of the central ring of tetra biphenyl corresponding to RSVRSF is 1223.4 cm$^{-1}$.

![Figure 9: Vibration form of ring stretching Raman frequency (A1/A1g) of odd and even linear acenes (a) Benzene ring stretching vibration, (b) Ring stretching vibration of central ring of anthracene, (c) Ring stretching vibration of central ring of Naphthalene](image)

Table 1: Theoretical calculations value of $E_{BL}$ (Kcal/mol), $E_{DB}$ (Kcal/mol), R and DOA of linear acenes central rings

<table>
<thead>
<tr>
<th>Molecular</th>
<th>R(whole)</th>
<th>R (central)</th>
<th>$E_{BL}$(whole)</th>
<th>$E_{DB}$(whole)</th>
<th>$E_{BL}$(central)</th>
<th>$E_{DB}$(central)</th>
<th>DOA(whole)</th>
<th>DOA(central)</th>
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<td>C6H6</td>
<td>1.394</td>
<td>1.394</td>
<td>20.1</td>
<td>969.4</td>
<td>20.1</td>
<td>969.4</td>
<td>0.01067</td>
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<td>C14H10</td>
<td>1.407</td>
<td>1.413</td>
<td>78.8</td>
<td>2271.8</td>
<td>87.9</td>
<td>1005.1</td>
<td>0.01749</td>
<td>0.04380</td>
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<td>C22H14</td>
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<td>1.418</td>
<td>134.5</td>
<td>3566.4</td>
<td>157.7</td>
<td>922.1</td>
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<td>1.413</td>
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<td>144.4</td>
<td>1925.7</td>
<td>0.02186</td>
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<td>430.3</td>
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<td>0.02152</td>
<td>0.15687</td>
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Structure, Stability and Aromaticity of Linear Acenes

Table 2: Theoretical calculation data of Raman frequency (cm$^{-1}$), imaginary frequency (NIF), aromaticity of central ring (NICS) and average bond length of C-C bond in central ring of linear acenes. NICS (min) refer to Minimum NICS value.

<table>
<thead>
<tr>
<th>Molecular</th>
<th>Point Group</th>
<th>NIF</th>
<th>$R_{cc}$(Å)</th>
<th>RSVRSF(cm$^{-1}$)</th>
<th>NICS(min)</th>
<th>NICS(0.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>$D_{2h}$</td>
<td>0</td>
<td>1.394</td>
<td>1011.5</td>
<td>-11.51(0.75)</td>
<td>-8.88</td>
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<tr>
<td>Triac</td>
<td>$D_{2h}$</td>
<td>0</td>
<td>1.413</td>
<td>1287.9</td>
<td>-14.46(0.75)</td>
<td>-11.90</td>
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<tr>
<td>Pentabenzene</td>
<td>$D_{2h}$</td>
<td>0</td>
<td>1.418</td>
<td>1331.3</td>
<td>-15.37(0.75)</td>
<td>-12.81</td>
</tr>
<tr>
<td>Hexabenzen</td>
<td>$D_{2h}$</td>
<td>0</td>
<td>1.421</td>
<td>1346.9</td>
<td>-15.87(0.75)</td>
<td>-13.32</td>
</tr>
<tr>
<td>Nine benzene</td>
<td>$D_{2h}$</td>
<td>0</td>
<td>1.423</td>
<td>1354.1</td>
<td>-16.13(0.75)</td>
<td>-13.58</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>$D_{2h}$</td>
<td>0</td>
<td>1.403</td>
<td>771.9</td>
<td>-11.88(0.75)</td>
<td>-9.23</td>
</tr>
<tr>
<td>Tetraphenylene</td>
<td>$D_{2h}$</td>
<td>0</td>
<td>1.413</td>
<td>1223.4</td>
<td>-14.46(0.75)</td>
<td>-11.89</td>
</tr>
<tr>
<td>Hexabenzen</td>
<td>$D_{2h}$</td>
<td>0</td>
<td>1.416</td>
<td>1269.9</td>
<td>-15.40(0.75)</td>
<td>-12.83</td>
</tr>
<tr>
<td>Octacene</td>
<td>$D_{2h}$</td>
<td>0</td>
<td>1.416</td>
<td>1297.4</td>
<td>-15.87(0.75)</td>
<td>-13.32</td>
</tr>
<tr>
<td>Decabenzene</td>
<td>$D_{2h}$</td>
<td>0</td>
<td>1.423</td>
<td>1318.8</td>
<td>-16.12(0.75)</td>
<td>-13.57</td>
</tr>
</tbody>
</table>

From the data in Table 2, we can see that the target molecule has no imaginary frequency and can exist stably. The NICS (0.0) is calculated at the central of the ring plane, and NICS (min) is calculated at a step of 0.25 Å to the minimum of NICS from 0.0 Å to 1.0 Å at the central of the ring plane. With the increase of benzene ring, the aromaticity of the central ring (NICS (min), NICS (0.0)) increases gradually, and the negative NICS value of the central ring of the target molecule is larger than the negative NICS value of benzene, that is, the aromaticity of the central ring of odd linear acenes is larger than that of single benzene ring. The RSVRSF value of the central ring increases with the increase of benzene ring. The order of RSVRSF increasing is consistent with that of aromaticity increasing. The aromaticity of the left and right rings (NICS (0.0) and NICS (min)) of even linear acenes increases with the increase of benzene rings. The RSVRSF value of the central ring of the target molecule is higher than that of the naphthalene ring. Therefore the NICS values of linear acenes are negative, i.e., the central rings of the target molecules are all aromatic molecules. The order of NICS (0.0) and NICS (min) values of even and odd linear acenes central rings increases with the increase of benzene rings, that is, the π aromaticity of even and odd linear acenes increases with the increase of benzene rings.

The comparison of theoretical Raman spectra and experimental Raman spectra of benzene, naphthalene and anthracene is shown in Fig. 10. It shows that there exist Raman peaks in the Raman spectra of benzene, naphthalene and anthracene. And the intensity of ring stretching vibration ($A_r$) Raman peaks in the Raman spectra is relatively large, which is beneficial to the experimental determination. The results of Fig. 10 show that the theoretical Raman spectra of the target molecule agree well with the experimental Raman spectra. It is theoretically predicted that the aromaticity of the target molecule can be determined by measuring the RSVRSF ($A_r/A_r$) experimentally. According to the molecular vibration equation, we can know that the vibration frequency of molecule is related to force constant, that is, the larger the force constant is, and the larger the vibration frequency is. The RSVRSF of odd linear acenes central ring (except base ring benzene) corresponding to the force constants of 2.87, 3.87, 4.7 and 5.61, respectively. The RSVRSF force constants of even linear acenes central ring (except base ring naphthalene) are 1.53, 2.28, 3.04 and 3.68, respectively. That is to say, the gradually increase of RSVRSF is consistent with the change of its frequency. The results showed that RSVRSF and aromaticity increased in the same order, that is, there was a correlation.

Stability and Aromaticity

Linear acenes are formed by the continuous addition of four carbon atoms formed by benzene. If each compound formed is equally stable, the energy change from one molecule to another should be consistent. The simplest method is to use thermo chemical derivative stabilization energy, which can reflect the activity of molecules, that is, the stability of molecules. Because the bond length of C=C is shorter than that of C-C bond, the interaction force between C=C bond is larger than that between C-C bond. The energy needed to open C=C bond is more than that of open C-C single bond. Therefore, the higher the DE/per value is, the worse the activity of the molecule and the better the stability of the molecule. Obtaining the aromaticity of the molecule is helpful to deduce the structure of the molecule and the activity of the molecule reaction. It can also be used to explain the stability of the aromatic system and to guide the synthesis of new functional substances. That is, the aromaticity of molecules is closely related to the stability of molecules.

$$DE = -627.51(E_{calc} + 232.25118 + (n-1)153.63813)$$

In the above formula, 627.51 is the conversion factor from Hartrees to kcal/mol, $E_{calc}$ is the energy calculated by molecule, 232.25118 is the energy of benzene, $n$ is the number of rings, and 153.638 13 is the energy difference between benzene and naphthalene.
Since linear acenes is formed by adding four carbon atoms to benzene continuously, the four carbon atoms of the linear acenes and the two carbon atoms of the previous linear acenes form a benzene ring, the calculated delocalization energy can represent the delocalization energy of one of the benzene rings of linear acenes. Because the interaction force of C-C bonds in linear acenes rings is basically unchanged, that is, the energy required to open the C-C bonds in each ring is almost equal. The calculated delocalization energy can be regarded as the delocalization energy of linear acenes central rings. The greater the delocalization energy is, the worse the activity of the molecules and the better the stability of the molecules. The value of DE/per reflects the stability of the whole molecule. The better stability of the molecule is, the larger the corresponding DE/per. The DE and DE/per of linear acenes are listed in Table 3.

<table>
<thead>
<tr>
<th>Molecular</th>
<th>DE (Kcal/mol)</th>
<th>DE/per (Kcal/mol)</th>
<th>DOA</th>
<th>NICS(0.0)</th>
</tr>
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<tbody>
<tr>
<td>C_{6}H_{6}</td>
<td>37.69</td>
<td>12.56</td>
<td>0.01067</td>
<td>-8.88</td>
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<tr>
<td>C_{10}H_{8}</td>
<td>62.46</td>
<td>12.49</td>
<td>0.02157</td>
<td>-9.23</td>
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<tr>
<td>C_{14}H_{10}</td>
<td>83.31</td>
<td>11.90</td>
<td>0.04380</td>
<td>-11.90</td>
</tr>
<tr>
<td>C_{18}H_{12}</td>
<td>102.63</td>
<td>11.40</td>
<td>0.06569</td>
<td>-11.98</td>
</tr>
<tr>
<td>C_{22}H_{14}</td>
<td>121.17</td>
<td>11.01</td>
<td>0.08506</td>
<td>-12.81</td>
</tr>
<tr>
<td>C_{26}H_{16}</td>
<td>139.36</td>
<td>10.72</td>
<td>0.09751</td>
<td>-12.83</td>
</tr>
<tr>
<td>C_{30}H_{18}</td>
<td>157.30</td>
<td>10.48</td>
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<td>-13.32</td>
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<tr>
<td>C_{34}H_{20}</td>
<td>175.14</td>
<td>10.30</td>
<td>0.15927</td>
<td>-13.32</td>
</tr>
<tr>
<td>C_{38}H_{22}</td>
<td>192.93</td>
<td>10.15</td>
<td>0.17632</td>
<td>-13.58</td>
</tr>
<tr>
<td>C_{42}H_{24}</td>
<td>202.45</td>
<td>9.64</td>
<td>0.27145</td>
<td>-13.57</td>
</tr>
</tbody>
</table>
Structure, Stability and Aromaticity of Linear Acenes

According to the data in table 3, it can be concluded that with the increase of the number of benzene rings, the corresponding DE value increases gradually, indicating that the stability of the central ring of linear acenes increases gradually. The process of increasing target molecule DE is the process of increasing the negative NICS and DOA of its central ring, and the process of increasing target molecule RSVRSF is also the process of increasing target molecule DE. Because the aromaticity of the molecule can be used to explain the stability of the molecule, that is, the aromaticity is directly related to the stability of the molecule, the linear acenes DE will gradually increase. From the value of DE/per, it can be concluded that the overall stability of linear acenes molecule decreases gradually. In addition to overlapping with each other, the p orbitals of two common carbons in linear acenes molecule overlap with the p orbitals of the other two adjacent carbons. Therefore, the closed large π bond electron cloud is not uniformly distributed on the naphthalene ring, which leading to the incomplete equivalence of C-C bond length. The aromaticity of linear acenes is worse than that of benzene. However, the value of DE/per of linear acenes molecule decreases gradually, that is, the stability decreases gradually. It also shows that the aromaticity of the molecule decreases gradually, and the DE/per is consistent with the electronic structure analysis of the molecule. The analysis shows that DE/per can be used to determine the aromaticity of molecules. DEs were correlated with DOA, RSVRSF and NICS. The stability DE of the central ring shows that RSVRSF and DOA have certain validity as new criterions for linear acenes. On the contrary, DE can not only determine the stability of molecular central rings, but also be used to judge the aromaticity of molecular central rings.

Correlation analysis

Fig. 2 shows the existence of σ and π in the target molecule. The formation of the electronic circulation is due to the existence of conjugate bonds within the molecule. The conjugate bonds are determined by the conjugate forces of equal size between atoms within the molecule. The vibration mode of the conjugate forces is the ring stretching vibration. So theoretically, there is a certain correlation between the aromaticity of the substance and the ring stretching vibration of the molecule. However, there are many types of ring stretching vibration of molecules. Group theory analysis shows that the ring stretching vibration of $A_{1g}$ symmetry type has strong Raman spectral activity, so there is a certain correlation between the aromaticity of molecules and the Raman spectral frequency of ring stretching vibration of $A_{1g}$ symmetry type. In order to further illustrate the validity of DOA as a new aromaticity criterion, it is necessary to analyze the correlation between DOA and aromaticity. Fig. 11 is a correlation curve drawn by Origin 8.0 between NICS, RSVRSF and DOA values of the central ring of the target molecule.

Fig 11 (a) shows that the correlation coefficients $R^2$ of central ring of odd linear acenes between RSVRSF($A1$) and NICS (min), NICS (0.0) are respectively 0.96 and 0.96. The correlation coefficients $R^2$ of central ring of even linear acenes between RSVRSF ($A1$) and NICS (min), NICS (0.0) are respectively 0.93 and 0.93. Fig 11 (b) shows the correlation coefficients $R^2$ of central ring of odd linear acenes between DOA and NICS (min), NICS (0.0) are respectively 0.89 and 0.89. The correlation coefficients $R^2$ of central ring of even linear acenes between DOA and NICS (min), NICS (0.0) are respectively 0.79 and 0.78. Fig 11 (c) shows that the correlation coefficients $R^2$ between RSVRSF ($A1$) and DOA of central ring of linear acenes are respectively 0.85(even) and 0.97(even). From the above analysis of aromaticity and Raman frequency of central ring of linear acenes, it can be seen that with the increase of benzene ring, the NICS value of the even and odd linear acenes central ring decreases gradually, that is, the aromaticity increases gradually. The RSVRSF of $A1g$ symmetric type of the corresponding central ring also increases gradually. The aromaticity of the central ring of linear acenes molecule is positively correlated with its RSVRSF. That is, the larger the RSVRSF of the molecule is, the greater the aromaticity. The DOA value and aromaticity of even and odd linear acenes central rings increase with the increase of the number of benzene rings. This is consistent with the conclusions of NICS and RSVRSF. It shows that DOA has certain validity as a new aromaticity criterion.

![Figure 11](image-url)

**Figure 11:** The correlation curves of RSVRSF ($A_{1g}$), DOA and NICS (min), NICS (0.0) of central ring of odd and even linear acenes (a) RSVRSF and NICS (b) DOA and NICS (c) RSVRSF and DOA
For planar or nearly planar molecules, these local contributions fall off rapidly at points above the ring centers where the π contributions dominate. Earlier statistical analyses indicated that isotropic NICS\(\pi z\)z values of related series of molecules may be even better measures of aromaticity than isotropic NICS(1) or NICS(0). Consequently, We have now analyzed the correlation between NICS\(\pi z\)z and RVSRSF, DOA values of target molecular central rings. Fig. 12 is a correlation curve drawn by Origin 8.0 between NICS\(\pi z\)z, RVSRSF and DOA values of the central ring of the target molecule.

Fig 12 (a) shows that the correlation coefficients R2 of central ring of odd and even linear acenes between NICS\(\pi z\)z and RVSRSF are 0.99 and 0.99, respectively. Fig 12 (b) shows the correlation coefficients R2 of central ring of odd and even linear acenes between NICS\(\pi z\)z and DOA are 0.95 and 0.99, respectively. From the above analysis of π aromaticity and Raman frequency of central ring of linear acenes, it can be seen that with the increase of benzene ring, the negative NICS\(\pi z\)z value of the even and odd linear acenes central ring increases gradually, that is, the π aromaticity decreases gradually. The RVSRSF of A1g symmetric type of the corresponding central ring increases gradually. With the increase of benzene ring, The NICS\(\pi z\)z decrease gradually is the RVSRSF and DOA increase gradually in the target molecule central ring. Hence RVSRSF and DOA can be used to evaluate the local aromaticity of target molecule.

Obtaining the aromaticity of molecule is helpful to deduce the structure, energy and activity of molecule reaction. It can also be used to explain the bonding characteristics, stability of aromatic system, predict the direction of reaction and guide the synthesis of new functional substances. The greater the aromaticity is, the more stable the substance, that is, the aromaticity of the substance determines the stability of the substance. Therefore, the aromaticity of substances is related to the stability of substance structure. Fig 13 is a correlation curve drawn between DE and RVSRSF, NICS and DOA of target molecule by Origin 8.0.

Fig. 13 is the correlation curve between the DE value of linear acenes and DOA, NICS, RVSRSF. In Fig. 13(c), the target molecule DE/per and DOA showed a correlation, and the R2 is 0.98 and 0.95, respectively. DE and DOA showed a positive correlation, that is, the target molecule increased with the increase of benzene ring, while the DOA value of central ring increased gradually. According to the value of DE, we can see that the stability of the molecular central ring increases gradually. From RVSRSF, NICS and DOA, we can see that the aromaticity of the central ring increases gradually. The rule between DE and aromaticity criterion is the same. Further analysis of the correlation between DE and aromaticity criterion by SPSS showed that the p values of both unilateral and bilateral tests were less than 0.05, that is, the correlation between the aromaticity of linear acenes central ring and DE was significant, indicating that DE had a significantly correlation with aromaticity. The larger the DE of linear acene is, the greater its aromaticity. It is believed that the aromaticity of the central ring and the stability of the target molecule can be estimated theoretically by calculating the size of DE, which provides a new theoretical basis for experimental measurement and theoretical calculation of the aromaticity of the target molecule. Since the interaction force between C=C bonds is greater than that between C-C bonds, that is, the stability of C=C is stronger than that of C-C bonds, the stability of linear acenes is mostly determined by C=C. Therefore, DE/per can be used to determine the stability of the whole molecule. The p orbitals of the two common carbons in linear acenes molecule overlap with each other, and they also overlap with the p orbitals on the two adjacent carbons. Therefore, the closed large π bond electron cloud is not uniformly distributed on the linear acenes.
ring, resulting in the incomplete equivalence of C-C bond length. The aromaticity of linear acenes is worse than that of benzene. Compared with benzene, the value of DE/per of linear acenes is smaller than that of monocyclic benzene, which indicates that the stability of linear acenes is worse than that of benzene. The structure analysis shows that the aromaticity of linear acenes is smaller than that of benzene, while the DE/per value of linear acenes is smaller than that of benzene. So the overall stability of linear acenes molecule is worse than that of benzene. It shows that DE/per is related to the aromaticity of linear acenes.

![Figure 13](image)

**Figure 13:** The correlation curves between DE and NICS, RSVRSF, DOA of odd and even linear acenes (a) DE and NICS (b) DE and RSVRSF (c) DE and DOA

**Conclusion**

In short, linear acenes are all planar structures of D2h point groups except benzene (benzene is D6h point group). And no imaginary frequency is a stable structure. Compared with benzene, the π aromaticity of linear acenes decreases. With the increase of benzene ring, the NICS value of the central ring is more negative and the π aromaticity of odd and even linear acenes decreases. When the NICS value of the central ring of the target molecule is more negative, the DOA value of the central ring becomes larger and larger, which indicates that the DOA of aromaticity of the target molecule is reliable to discriminate the aromaticity of the target molecule by considering both geometric and energy factors in theory. The calculation results of RSVRSF and NICS of central ring of odd and even linear acenes show that the RSVRSF (A1) of central ring is highly correlated with the aromaticity (NICS), π aromaticity (NICSzz). In theory, RSVRSF with A1 symmetry exists in linear acenes compounds, and Raman spectra are very strong. In experiments, there are also ring stretching vibration absorption peaks in benzene, naphthalene and anthracene with high A1 symmetry. It is theoretically predicted that we can predict the aromaticity of the central ring of linear acenes by measuring the RSVRSF of the central ring in experiments, and realize the determination of the aromaticity of the central ring of the target molecule in experiments. The correlation analysis of DE with NICS, DOA and RSVRSF shows that NICS, DOA and RSVRSF are highly correlated with DE, and the correlation coefficients are very large. Theoretical prediction of DE can not only determine the stability of the central ring of the target molecule, but also predict the aromaticity of the central ring by calculating the size of the target molecule DE. The larger the molecular DE is, the greater the aromaticity of the central ring. DE/per results show that the overall stability of the molecule decreases gradually, that is, the aromaticity decreases gradually.

In conclusion, DE/per can be used to judge the aromaticity of molecules on the basis of determining the overall stability of molecules. An aromaticity index DOA, which takes into account both geometric and energy factors, can be applied to determine the aromaticity of the central ring in linear acenes molecules. It is predicted that the aromaticity of the central ring of the target molecule can be quantitatively determined by measuring the RSVRSF size of A1g/A1 symmetry. The larger the RSVRSF, the greater the aromaticity of the target molecule central ring is, the smaller the π aromaticity of the target molecule central ring is. Molecular aromaticity determines the stability of the molecule, and in turn, the stability can predict the aromaticity of the molecule. In other words, DE can not only explain the stability of the molecular central ring, but also predict the aromaticity of the central ring. It provides a theoretical reference for the determination of the aromaticity of the central ring of the target molecule by using the ring stretching vibration raman spectral frequency.

**References**