

A thorough theoretical exploration of intriguing characteristics of cyclo[18]carbon: Geometry, bonding nature, aromaticity, weak interaction, reactivity, excited states, vibrations, molecular dynamics and various molecular properties

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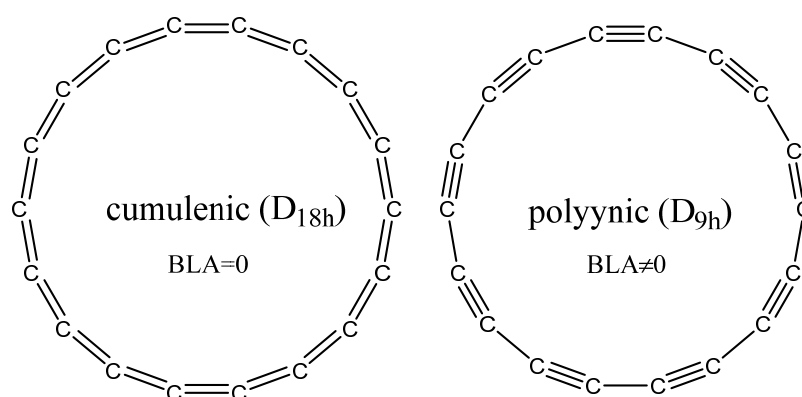
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Abstract: Although cyclo[18]carbon has been theoretically and experimentally investigated since long time ago, only very recently it was prepared and directly observed by means of STM/AFM in condensed phase (Kaiser *et al.*, *Science*, **365**, 1299 (2019)). The unique ring structure and dual 18-center π delocalization feature bring a variety of unusual characteristics and properties to the cyclo[18]carbon, which are quite worth to be explored. In this work, we present an extremely comprehensive and detailed investigation on almost all aspects of the cyclo[18]carbon, including (1) Geometric characteristics (2) Bonding nature (3) Electron delocalization and aromaticity (4) Intermolecular interaction (5) Reactivity (6) Electronic excitation and UV/Vis spectrum (7) Molecular vibration and IR/Raman spectrum (8) Molecular dynamics (9) Response to external field (10) Electron ionization, affinity and accompanied process (11) Various molecular properties. We believe that our full characterization of the cyclo[18]carbon will greatly deepen researchers' understanding of this system, and thereby help them to utilize it in practice and design its various valuable derivatives.

Keywords: chemical bond; electron delocalization; aromaticity; weak interaction; π - π stacking; ab-initio molecular dynamics; IR spectrum; Raman spectrum; UV-Vis spectrum; excited state; electron localization function; localized molecular orbital; bond order; atoms-in-molecules; Multiwfn; wavefunction analysis; induced ring current; electrostatic potential; average local ionization energy; hyperpolarizability; ionization energy; electron affinity

1. Introduction

The cyclo[18]carbon is a ring consisting of 18 carbon atoms. The unique geometry and electronic structure of this system has sparked a lot of interests among researchers. The earliest research on the cyclo[18]carbon began with a paper published by Hoffman in 1966.^[1] After that, many research articles related to the cyclo[18]carbon have been published, the research topics cover geometry, energy,^[2-4] electron correlation,^[5] aromaticity,^[6] tunneling effect^[7] and so on.^[8] It is worth noting that the structure of this system was subject to long-term debates. It is common belief that the cyclo[18]carbon has two possible structures, are shown in Scheme 1.



Scheme 1 Two possible structures of cyclo[18]carbon. The BLA denotes bond length alternation.

Despite that there have been strong evidences for the existence of the cyclo[18]carbon in gas phase, the cyclo[18]carbon was experimentally observed in condensed phase only very recently. In ref. [9], the authors employed scanning tunneling microscopy (STM) and atomic force microscopy (AFM) techniques to characterize the cyclo[18]carbon prepared on bilayer NaCl on Cu(111) surface at 5 Kelvin and they argued that cyclo[18]carbon has "alternating triple and single bonds". This work provides a very strong evidence that the cyclo[18]carbon belongs to polyynic structure.

It is foreseeable that the first experimental observation of the cyclo[18]carbon will bring a new round of research boom of this and analogous systems, since the cyclo[18]carbon and its derivatives may have a wide range of applications in the future. We believe it is important to have a full characterization of various aspects of the cyclo[18]carbon, thereby deepening the researchers' understanding of this system, and finally help them to utilize the cyclo[18]carbon in practice and design its various valuable derivatives. Quantum chemistry has become a very mature and reliable tool for exploring wide variety of molecular features, the present article will present a very comprehensive theoretical study of various aspects of the cyclo[18]carbon, its geometric structure, bonding nature, electron delocalization, intermolecular interaction, aromaticity, reactivity, excited states, molecular vibration, dynamic behavior and so on will be subjected to our analysis and discussion.

2. Computational Details

Unless otherwise specified, all calculations involved in this work were carried out via ωB97XD

exchange-correlation functional^[10] in conjunction with def2-TZVP basis set^[11] in vacuum. As will be shown later, since ω B97XD can well reproduce the geometry yielded by the more robust coupled-cluster singles and doubles (CCSD) theory,^[12] it is anticipated that ω B97XD can also reasonably represent electronic structure and potential energy surface (PES) of the cyclo[18]carbon. Gaussian 16 A.03 code was employed for all quantum chemistry calculations.^[13]

Unless explicitly noted, all analyses as well as drawing of various kinds of maps were finished via the Multiwfn 3.7(dev) code^[14] developed by us, which can be freely obtained at the official site <http://sobereva.com/multiwfn>. Some isosurface maps were rendered by means of VMD visualization program^[15] based on the files exported by Multiwfn.

Most molecular structure maps and vibrational mode maps were plotted by GaussView 6.0.16.^[16]

The ACID induced current ring analysis^[17] was realized by ACID code^[18] based on the output file of Gaussian, the map was finally generated by POV-Ray render.^[19] GIMIC analysis was finished by GIMIC code^[20] based on the formatted check point file of Gaussian.

Symmetry-adapted perturbation theory (SAPT) was carried by PSI4 1.2 code.^[21]

Molecular dynamics trajectories were simulated by ORCA 4.2.1 code^[22] and visualized by VMD. The RIJCOSX technique^[23] was enabled to significantly accelerate the calculation. The ω B97X-D3^[24] functional was employed instead of the ω B97XD because the latter is not supported by the ORCA program. Since the ω B97X-D3 does not differ to its predecessor ω B97XD significantly, it is expected that the ω B97X-D3 can also reasonably represent PES of the cyclo[18]carbon and thus yield correct dynamics trajectories. In the simulation, the step size was set to 1 fs, Berendsen thermostat^[25] with time constant of 20 fs was employed to control the temperatures.

3. Results and Discussion

Bond lengths and impact of calculation level

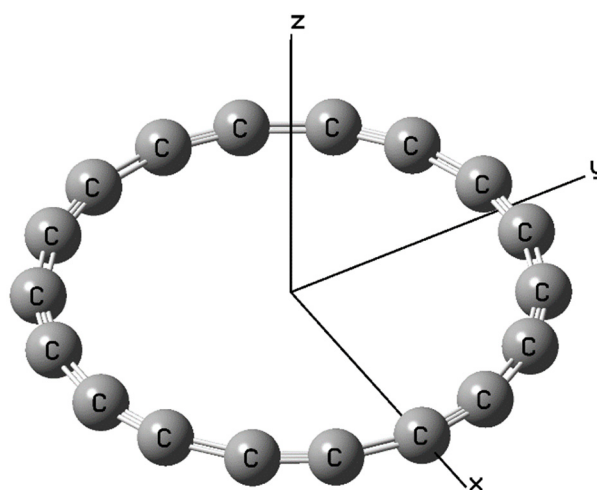


Fig. 1 Optimized geometry of cyclo[18]carbon at ω B97XD/def2-TZVP level.

The optimized geometry of the cyclo[18]carbon at the ω B97XD/def2-TZVP level is shown in Fig. 1. For comparison purpose, the bond lengths optimized at different levels are presented in Table 1, note that under all cases the geometry is exactly planar. As experimentally determined in ref. [9], this molecule has two kinds of bonds with different lengths. From Table 1 it can be seen that ω B97XD, MN15,^[26] M06-2X^[27] and BHandHLYP^[28] functionals result in bond length alternation phenomenon. This kind of geometry corresponds to D_{9h} point group and is known as polyynic structure.^[4] In contrast, the very commonly used B3LYP,^[29] PBE0^[30], HSE06^[31] as well as TPSSh^[32] functionals result in fully equalized bond lengths, this kind of geometry has point group of D_{18h} and is known as cumulenic structure.^[4] Obviously, since they are unable to reproduce the AFM/STM experimental observation in ref. [9], they should not be employed in any study of the cyclo[18]carbon and its derivatives.

Table 1 Bond lengths (Å) of two kinds of bonds of cyclo[18]carbon optimized at different calculation levels

Method	HF exchange ^a	Basis set	R1	R2	BLA ^b
TPSSh	10%	def2-TZVP	1.279	1.279	0.000
B3LYP	20%	def2-TZVP	1.277	1.277	0.000
HSE06	25~0%	def2-TZVP	1.276	1.276	0.000
PBE0	25%	def2-TZVP	1.276	1.276	0.000
MN15	44%	def2-TZVP	1.233	1.338	0.106
BHandHLYP	50%	def2-TZVP	1.214	1.337	0.123
M06-2X	54%	def2-TZVP	1.223	1.345	0.122
ω B97XD	22.2~100%	def2-TZVP	1.221	1.344	0.123
ω B97XD	22.2~100%	def-TZVP	1.221	1.344	0.123
RCCSD	/	def-TZVP	1.220	1.368	0.148
UCCSD	/	def-TZVP	1.215	1.371	0.156
GFN2-xTB	0%	/	1.276	1.276	0.000
PM7	/	/	1.226	1.351	0.125

^a Hartree-Fock exchange composition. For range-separated functionals, the values before and after the ~ symbol are the compositions in short and long ranges of interelectronic interaction, respectively.

^b Bond length alternation, namely R2 minus R1

From Table 1, it can be seen that the bond length alternation character has close relationship with the Hartree-Fock exchange (HFX) composition in exchange-correlation (XC) functionals. Indeed, our recent comprehensive benchmark of XC functionals (to be published) shows that BLA of the present system has strong positive correlation with HFX. It was found that BLA produced by all pure functionals is exactly zero. Among all known XC functionals, the functional with lowest global HFX composition that can give nonvanishing BLA character is PBE0-1/3,^[33] which has HFX of 33.3%. However the BLA produced by PBE0-1/3 is merely 0.066Å, which is significantly underestimated if compared to the CCSD result.

It is worth to note that in the supplemental material of ref. [9], the authors presented optimized geometry of the cyclo[18]carbon by HSE functional via FHI-aims code, the short and long C-C bonds have lengths of 1.195 and 1.343 Å, respectively. Their data seems to contradict our data in Table 1, in which the HSE06 functional gives equalized bond length of 1.277 Å. The remarkable

difference comes from the fact that the HFX in the HSE functional employed in ref. [9] was artificially set to 80%, which is an extremely high value, therefore it is naturally expected that their calculation must yield quite large BLA.

CCSD/def-TZVP is the best level that we can afford to optimize the cyclo[18]carbon. It is important to mention that the restricted Hartree-Fock (RHF) wavefunction is an unstable solution to the current system, hence unrestricted Hartree-Fock (UHF) wavefunction generated by symmetry-broken treatment may be a more reasonable reference state for the CCSD calculation. With this in mind, we optimized the geometry via both restricted CCSD (RCCSD) and unrestricted CCSD (UCCSD) theories. From Table 1 one can see that RCCSD and UCCSD results are quite similar, both of them correspond to polynic structure with BLA of 0.15 Å.

Currently, high resolution experimental data of the cyclo[18]carbon geometry is not available. Since CCSD is a method not only accurate but also robust for geometry optimization purpose, our CCSD/def-TZVP data can be regarded as the best estimation of the cyclo[18]carbon structure in vacuum. The CCSD data can also be used to judge the rationality of DFT calculations. A comparison of optimized bond lengths between ω B97XD/def-TZVP and UCCSD/def-TZVP levels shows that ω B97XD can nicely reproduce geometry character of the cyclo[18]carbon, the deviation in R1 and R2 between the two levels are only 0.006 and -0.027 Å, respectively, which are small enough to be ignored, demonstrating that ω B97XD is one of the best choices in the available XC functionals for studying the cyclo[18]carbon. Table 1 also shows that the geometries optimized by ω B97XD in conjunction with the medium-sized def-TZVP and more expensive def2-TZVP basis sets are indistinguishable, implying that the inexpensive ω B97XD/def-TZVP level is already well-suited for exploring characteristics of the cyclo[18]carbon and analogous systems.

We also tested two extremely cheap methods, including the well-known semi-empirical method PM7^[34] and the recently proposed GFN2-xTB theory,^[35] the latter may be viewed as a semi-empirical variant of the Kohn-Sham density functional theory. Despite that GFN2-xTB works well for many chemical systems, from Table 1 it can be seen that GFN2-xTB is unable to describe structure of the cyclo[18]carbon qualitatively correctly, just like all pure functionals. The BLA value given by PM7 looks as reasonable as ω B97XD, however, attention should be paid to the fact that correctly predicting PES minimum point does not necessary mean the method is able to faithfully represent the whole PES. Given that PM7 is only a very crude empirical approximation of *ab-initio* methods, whether or not PM7 is able to qualitatively describe chemical reactions as well as intermolecular interactions for the cyclo[18]carbon and its analogues is highly questionable.

Based on the ω B97XD/def2-TZVP geometry and the wavefunction at the corresponding level, we plotted electron density map above 1 Å of the molecular plane, see Section S1 of supplemental material. It can be seen that the simulated map can well reproduce basic characteristics of the experimental AFM image presented in ref. [9].

Molecular size

Bader suggested employing $\rho = 0.001$ a.u. isosurface as definition of molecular van der Waals (vdW) surface,^[36] which has been widely accepted in the computational chemistry community. Based on this definition, we quantified molecular size for the cyclo[18]carbon, as shown in Fig. 2. The calculated van der Waals surface area is 281.1 Å², the molecular vdW volume is 271.4 Å³. It is worth to note that the inner diameter of the cyclo[18]carbon (3.44 Å) is comparable to the diameter

of Ar atom (3.94 Å) calculated in the same manner

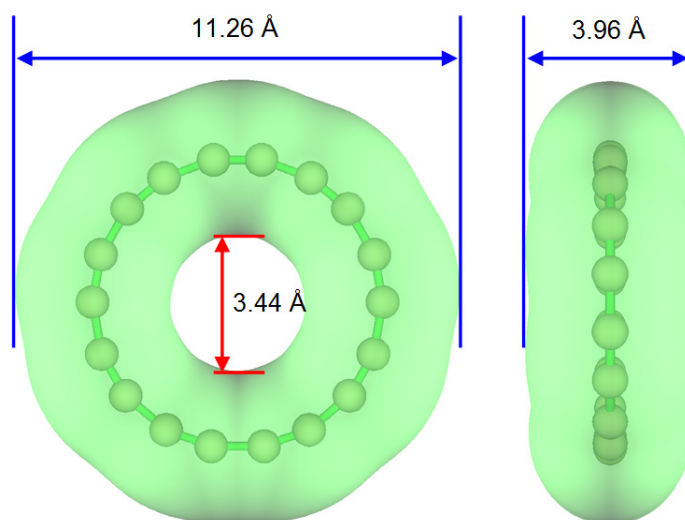


Fig. 2 Inner diameter, outer diameter and thickness of cyclo[18]carbon. $\rho = 0.001$ a.u. is used to define the molecular van der Waals surface.

Molecular kinetic diameter is a quantity frequently involved in the discussion of gas adsorption and permeation in porous and polymeric materials. Ref. [37] defined a novel way of evaluating kinetic diameter based on quantum chemistry calculation, namely constructing isosurface of $\rho = 0.0015$ a.u. based on PBE0/def2-TZVP^[11,30] wavefunction and then measuring the distance between the two surface vertices farthest apart. We employed this method to calculate kinetic diameter for the cyclo[18]carbon, the result is 5.47 Å, which can be used as a reference when designing porous materials to separate the cyclo[18]carbon molecules.

Molecular orbitals and density-of-states

Molecular orbitals (MOs) of the cyclo[18]carbon can be divided as three sets, namely eighteen σ MOs, nine in-plane π MOs and nine out-plane π MOs. Occupied π MOs are plotted as Figs. S2 and S3. As can be seen from the figures, the out-plane π MOs have nodal plane along the ring plane, they have similar feature to the π MOs of conjugated organic systems, such as 18-annulene. In contrast, the in-plane π MOs fully stem from the unique geometric and electronic structures of the cyclo[18]carbon and thus they are not observed in any organic system.

Density-of-states (DOS) map is able to vividly exhibit distribution of MO levels.^[14,38,39] The DOS curve reflects number of MOs in unit energy interval at corresponding energy. We plotted total DOS (TDOS) map and the partial DOS (PDOS) maps contributed by the three different sets of MOs for the cyclo[18]carbon, as shown in Fig. 3. We refer this kind of map as MO-PDOS map.

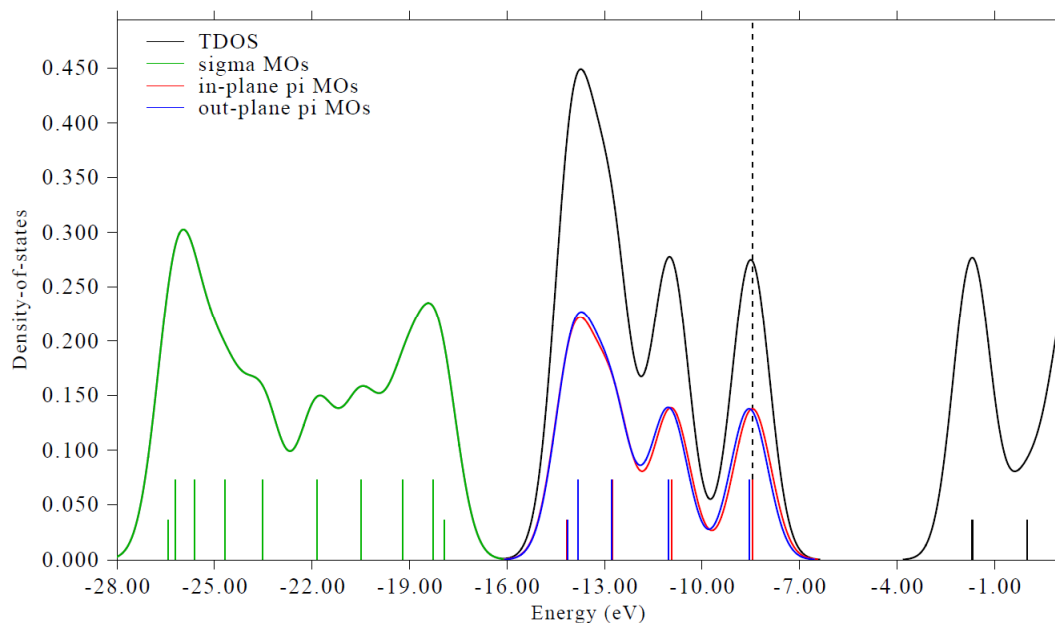


Fig. 3 MO-PDOS map of cyclo[18]carbon. Black curve corresponds to total DOS, while green, red and blue curves correspond to partial DOSs due to occupied σ MOs, in-plane π MOs and out-plane π MOs, respectively. The dashed line highlights the position of HOMO. The half and full heights of the spikes correspond to degeneracy of 1 and 2, respectively.

From Fig. 3 one can clearly see that the σ MOs have much lower energies than the π MOs, however, the in-plane and out-plane π MOs have nearly indistinguishable energies, this is why their corresponding PDOS curves almost overlap with each other. This observation implies that the two kinds of π MOs have very similar intrinsic features. From the height of the spikes in Fig. 3, it can be seen that because of the high-order point group of the cyclo[18]carbon (D_{9h}), most of the MOs show double degenerate character.

At the current ω B97XD/def2-TZVP level, the energy of the HOMO and LUMO of the cyclo[18]carbon is found to be -8.45 and -1.70 eV, respectively, corresponding to HOMO-LUMO gap of 6.75 eV.

Nature of the C-C bonds

The nature of the C-C bonds in the cyclo[18]carbon is of great interest due to its unique electronic structure. It is commonly believed that the cyclo[18]carbon has "alternating triple and single bonds",^[9] however, is it really true?

Table 2 Bond order calculated by various methods

	considered MOs ^a	short C-C	long C-C	Diff. ^b
	All MOs	2.568	1.256	1.313
Mayer bond order	in-plane π MOs	0.715	0.168	0.547
	out-plane π MOs	0.714	0.188	0.526
	σ MOs	1.153	0.881	0.272
	Fuzzy bond order	2.283	1.428	0.856
	Wiberg bond order ^c	2.359	1.521	0.838
	Wiberg bond order (NAO based) ^d	2.360	1.310	1.050
	Laplacian bond order	2.451	1.696	0.756

^a The orbitals taken into account in the calculation of Mayer bond order

^b The difference between the short and long bonds

^c Calculated based on the basis functions generated by Löwdin orthogonalization

^d Calculated based on natural atomic orbitals^[40]

In order to demystify the bonding nature, we first calculated bond orders, see Table 2. Several different bond order definitions were taken into account, including Mayer bond order,^[41] Fuzzy bond order,^[42] Wiberg bond order^[43] and the Laplacian bond order^[44] proposed by us. Essentially the first three kinds of bond orders reflect the average number of electron pairs shared by two atoms,^[45] while the Laplacian bond order is obtained by integrating negative part of Laplacian of electron density in the bonding region and was shown to be able to faithfully represent actual bonding strength.^[44] From Table 2 one can see that none of the calculated bond orders support the argument that the cyclo[18]carbon has alternating single and triple bonds, because the bond orders deviate from 1.0 and 3.0 evidently for the long and short bonds, respectively. Since a σ bond can at most contribute 1.0 to the bond order, the long C-C bond in the cyclo[18]carbon should not be simply viewed as a single bond but should be considered to be accompanied by a certain degree of π character. Clearly, using the Lewis structure containing alternating single and triple bonds to represent bonding character for the cyclo[18]carbon, as illustrated in the right part of Scheme 2, is qualitatively wrong. We strongly suggest using "alternating bonds" instead of the quite misleading "alternating triple and single bonds" when referring to the cyclo[18]carbon.

Decomposing Mayer bond order allows us to gain deeper insight into the contribution of different MOs to bonding. In Table 2 we also listed contributions from the in-plane π MOs, out-plane π MOs and σ MOs. Notice that in principle the Mayer bond order cannot be exactly decomposed as contributions of various orbitals, however since the coupling between the three kinds of MOs of the cyclo[18]carbon is fairly weak, the sum of their contributions is very close to the total Mayer bond order. From the data in Table 2 it can be seen that for the short C-C bonds, both in-plane and out-plane π MOs have significant and equal contributions, while for the long C-C bonds, the contribution due to the π MOs is by far lower than the case of short C-C bonds, showing that π interaction plays an evidently weaker role in the long C-C bonds. In addition, the contribution due to the σ MOs exhibits that the bonding effect contributed by σ interaction in the long C-C bonds is also weaker than the short C-C bonds.

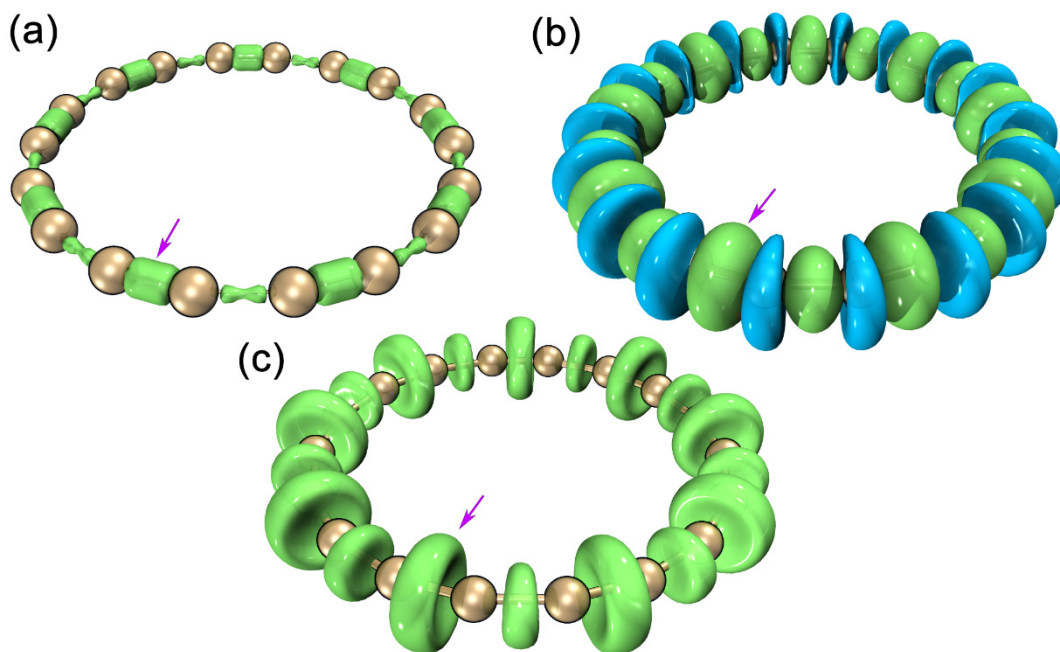


Fig. 4 Isosurface map of three real space functions of cyclo[18]carbon (a) Valence electron density with isovalue of 0.32 a.u. (b) Deformation of electron density with isovalue of 0.01 a.u., green and blue correspond to positive and negative regions, respectively (c) Electron localization function with isovalue of 0.8. A short C-C bond in each map is highlighted by an arrow.

There are many available real space functions that can characterize chemical bonds.^[46] Isosurface maps of valence electron density (ρ_{val}),^[46] deformation density (ρ_{def})^[46] and electron localization function (ELF)^[47,48] of the cyclo[18]carbon are given in Fig. 4. The ρ_{val} corresponds to the electron density with removal of contribution of inner core electrons, in Ref [46] it is well demonstrated that this function is quite useful in characterizing chemical bonds. From the ρ_{val} shown in Fig. 4(a) it can be seen that amount of valence electrons distributed around the short C-C bonds is by far richer than that around the long C-C bonds, this is an evident signal that short C-C bond is much stronger. The ρ_{def} is defined as $\rho - \sum_A \rho_A^{\text{free}}$, where ρ is actual molecular electron density while ρ_A^{free} is spherically averaged electron density of atom A in its isolated state. The green isosurfaces in Fig. 4(b) vividly exhibited that there are significant increase of electron density in the bonding regions during formation of the system from isolated atoms, this is a typical observation of the systems consist of covalent bonds. The isosurface of ρ_{def} is detectably fatter around the short C-C bonds than the long C-C bonds, showing larger amount of electron density was moved towards the corresponding bonding region during formation of the bonds. ELF is a function that measures degree of electron localization in different molecular regions. Shape of ELF isosurface of single bond, double bond and triple bond are remarkably different, as illustrated in Fig. S4. From the acetylene case it can be seen that the representative character of a bond consists of a typical σ interaction and two pairs of π interactions is that the shape of ELF isosurface is torus. From Fig. 4(c) it is seen that the ELF isosurfaces for both kinds of C-C bonds look like torus, this is a direct evidence that double π interactions participate in both the short and long C-C bonds. However, the ELF isosurface for the former is conspicuously wider than the latter, reflecting that short C-C bonds have much stronger π interaction.

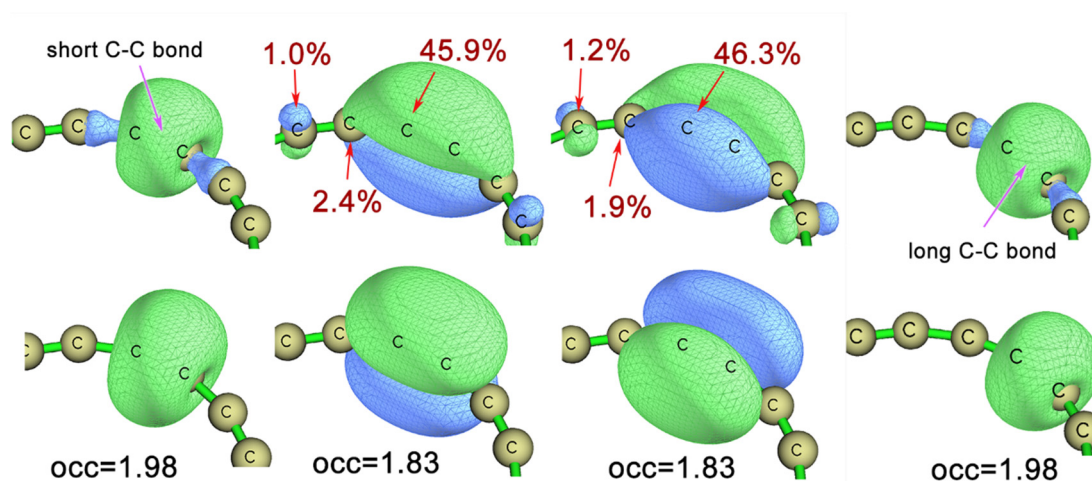


Fig. 5 Isosurface map of all unique Pipek-Mezey localized molecular orbitals (LMOs, upper maps) and pre-orthogonal natural bond orbitals (PNBOs, lower maps) of cyclo[18]carbon. Isovalue is set to 0.03, green and blue correspond to positive and negative orbital phases, respectively. Atomic contributions to the LMOs calculated by Mulliken method are labelled, "occ" denotes occupation number of the PNBOs.

The bonding character of the cyclo[18]carbon can also be studied in terms of orbitals. The MOs of this system show global delocalization character and thus are unable to be mapped to individual C-C bonds. However, after performing unitary transformation for the MOs by orbital localization method, the resulting localized molecular orbitals (LMOs) show very close relationship with the C-C bonds, as shown in the upper part of Fig. 5. This figure contains all unique LMOs generated by the Pipek-Mezey algorithm^[49] and shows orbital compositions computed by the Mulliken method.^[50] It can be seen that among the first three plotted LMOs, one shows typical σ character while the other two show π character, all of them fully cover one of the short C-C bonds, this explains the reason why short C-C bond has a bond order evidently higher than 2.0 (Table 2). For each long C-C bond, there is only a σ LMO that mainly covers its bonding region, this is why its bond order is much smaller compared to the short C-C bonds. Notice that the π LMOs display nonnegligible spatial delocalization, that is their tails extended to the neighbouring atoms to some extent, as quantitatively revealed by the calculated orbital compositions in Fig. 5. This orbital delocalization effect leads to the long C-C bonds also exhibit partial π characteristics.

The pre-orthogonal natural bond orbital (PNBO) defined in the natural bond orbital (NBO) theory^[51] provides another viewpoint about the bonding. All the four PNBOs shown in the lower part of Fig. 5 are pure two-center orbitals, the first three (one σ and two π types) completely correspond to a short C-C bond, while the last one fully corresponds to a long C-C bond. The occupation number of the two π type of PNBOs deviates from ideal value of closed-shell orbital (2.0) prominently, sufficiently reflecting that the short C-C bonds in the cyclo[18]carbon cannot be viewed as triple bonds in the strict sense. The occupation deviation from integer is essentially caused by electron delocalization, whose role in the present system can never be underestimated.

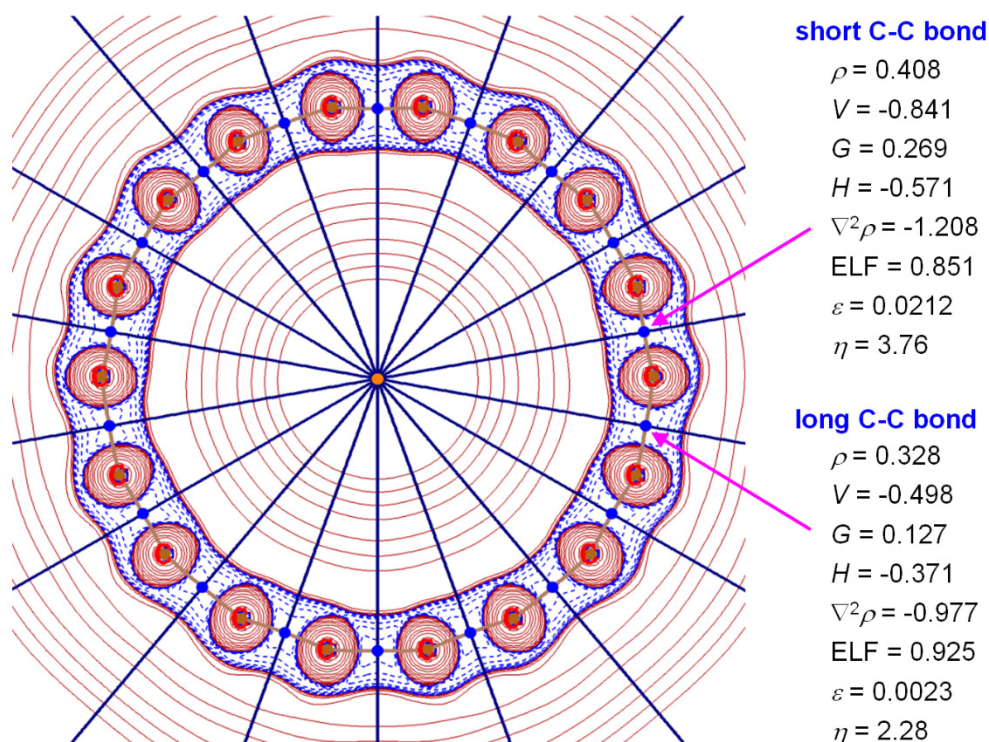


Fig. 6 Contour line map of Laplacian of electron density ($\nabla^2\rho$) in the cyclo[18]carbon ring plane, red solid lines and blue dashed lines represent positive and negative regions, respectively. Blue points and orange point correspond to position of bond critical points (BCPs) and ring critical point (RCP), respectively. Dark blue lines portray interbasin surfaces between atomic basins. Values of some real space functions at the BCP are given, including ρ (electron density), V (potential energy density), G (Lagrangian kinetic energy density), H (energy density), $\nabla^2\rho$, ELF, ε (ellipticity of electron density) and η (eta index).

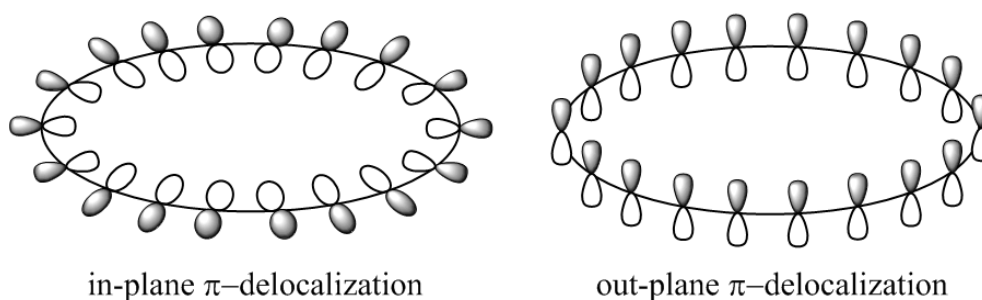
The atoms-in-molecules (AIM) theory is quite popular in investigation of interatomic interactions.^[38,52] In this theory, bond critical point (BCP) is viewed as the most representative point in an interaction path, therefore properties at this point can be used to characterize a bond. In addition, in the framework of AIM, the Laplacian of electron density ($\nabla^2\rho$) is often employed in discriminating covalent and non-covalent interactions.^[44] Fig. 6 presents contour line map of $\nabla^2\rho$ in the cyclo[18]carbon ring plane and provides value of many real space functions calculated at the BCPs of the C-C bonds. First, from Fig. 6 one can observe that in the bonding regions the $\nabla^2\rho$ is evidently negative, which strongly demonstrates the covalent nature of the C-C bonds. This point is also reflected in the large Laplacian bond orders shown earlier. The BCPs corresponding to the short C-C bonds have considerably larger ρ and more negative of potential energy density (V) and energy density (H) than the long C-C bonds, these observations further exhibit the prominent difference in bonding strength of the two kinds of bonds in the cyclo[18]carbon. As a comparison, BCP properties corresponding to the C-C bond in ethane are calculated, the result are $\rho = 0.241$ a.u., $V = -0.261$ a.u. and $H = -0.204$ a.u.; by comparing which to the data in Fig. 6 it is found that even the long C-C bonds in the cyclo[18]carbon are stronger than the C-C bond in ethane.

The ellipticity of electron density (ε)^[53] at BCP is an indicator of asymmetric distribution of electron density around the bond axis, the higher deviation to axisymmetric distribution, the larger

the ε value at the BCP. For example, the ε at the BCP of the C-C bond in ethene is quite large (about 0.45), while the value of the C-C bond in ethane and acetylene is exactly zero. As shown in Fig. 6, the ε at the BCP corresponding to both kinds of C-C bonds in the cyclo[18]carbon is quite close to zero, implying that the in-plane π and out-plane π interactions have nearly equal contributions to the bonding.

It was argued that the η (eta index) at BCP is less than unity for closed-shell interactions and increases with increasing covalent character.^[54] This index at the BCPs of the short and long C-C bonds is 3.76 and 2.28, respectively, which further prove the strong covalent nature of these bonds.

Global electron delocalization



Scheme 2 Origin of the two kinds of π electron delocalization in cyclo[18]carbon.

The double 18-center π electron delocalization character of the cyclo[18]carbon is illustrated in Scheme 2 and has been recognized since long time ago.^[6,9] It is common belief that the in-plane π and out-plane π global delocalizations stem from overlap between the p atomic orbitals parallel and perpendicular to the ring, respectively. The electron delocalization may be the most fascinating feature of the cyclo[18]carbon, therefore it is important to carry out an in-depth examination in its nature.

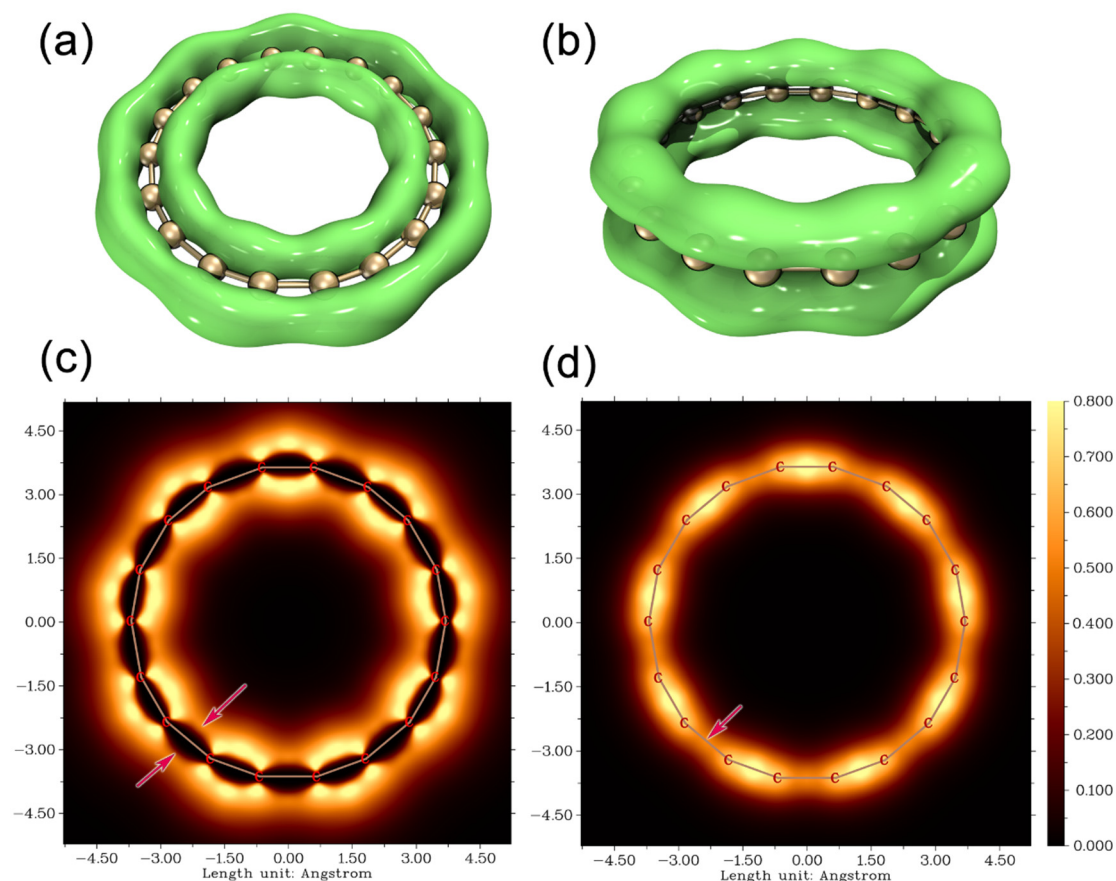


Fig. 7 Localized orbital locator calculated based on in-plane π MOs (left side, $\text{LOL-}\pi_{\text{in}}$) and out-plane π MOs (right side, $\text{LOL-}\pi_{\text{out}}$) of cyclo[18]carbon. (a) and (b) correspond to isosurface maps of $\text{LOL-}\pi = 0.2$, (c) shows $\text{LOL-}\pi_{\text{in}}$ in the ring plane, (d) shows $\text{LOL-}\pi_{\text{out}}$ above 1 Bohr of the ring plane.

The localized orbital locator^[55] calculated based on π orbitals ($\text{LOL-}\pi$) is a quite useful function in revealing delocalization path of π electrons. For example, recently we employed it to unravel the electron delocalization nature of macrocyclic[32]Octaphyrin(1.0.1.0.1.0.1.0).^[56] We respectively calculated $\text{LOL-}\pi$ for the in-plane π MOs and out-plane π MOs, which will be referred to as $\text{LOL-}\pi_{\text{in}}$ and $\text{LOL-}\pi_{\text{out}}$, respectively. Their isosurface maps are given as Figs. 7(a) and 7(b), which very vividly outline the favorable delocalization channels of the electrons in the in-plane π MOs and out-plane π MOs. In order to better exhibit distribution of $\text{LOL-}\pi_{\text{in}}$ and $\text{LOL-}\pi_{\text{out}}$, we also plotted color-filled map for the $\text{LOL-}\pi_{\text{in}}$ in the ring plane and the $\text{LOL-}\pi_{\text{out}}$ above 1 Bohr of the ring, as shown in Figs. 7(c) and 7(d), respectively. From the color it can be seen that although the global π electron delocalization is undoubtedly formed, the delocalization is slightly hindered in the π region of the long C-C bonds (indicated by red arrows in the figure), because the $\text{LOL-}\pi$ in these regions is detectably lower than the surrounding regions.

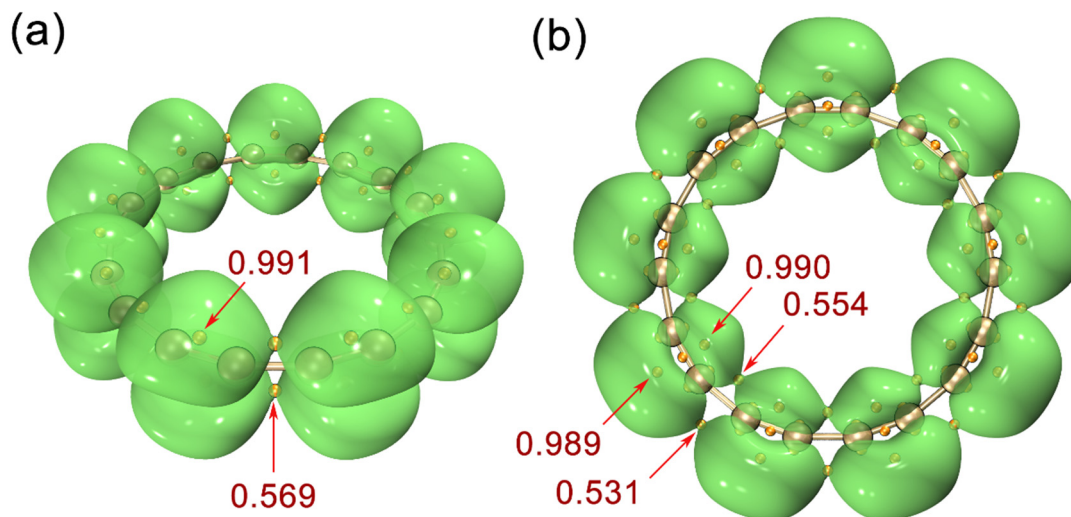


Fig. 8 Isosurface map of electron localization function (ELF) calculated based on (a) out-plane π MOs and (b) in-plane π MOs of cyclo[18]carbon. The isovalue is set to 0.569 and 0.531 in (a) and (b), respectively. Bifurcation points of ELF are plotted as orange spheres, the bifurcation values are labelled.

ELF- π is another useful function in revealing major π electron delocalization paths,^[57] it corresponds to the ELF calculated by only taking π orbitals into account. In Refs. [58] and [59], it is shown that values of ELF- π at its bifurcation points can be used to quantify strength of π conjugation. The so-called bifurcation point of ELF- π is mathematically defined as (3,-1) type of critical point of this function, it corresponds to the position where a ELF- π isosurface just started to split as two. It is believed that the higher the ELF- π value at a bifurcation point, the more easily the π electrons delocalize between the two ELF domains linked by this point. The isosurfaces as well as bifurcation points of ELF- π calculated for out-plane and in-plane π electrons are shown as Figs. 8(a) and 8(b), respectively. From the labelled values it is quite obvious that irrespective of the in-plane or out-plane type of the π electrons, the π conjugation over the long C-C bonds is by far weaker than over the short C-C bonds, since the bifurcation value of the latter case is quite close to theoretical upper limit of the ELF- π (1.0), while for the former case the value is merely between 0.5 and 0.6. For comparison purpose, we also computed ELF- π bifurcation value for benzene and ethene at the same level, the result is 0.895 and 1.000, respectively. It is seen that strength of both in-plane and out-plane π electron delocalizations at the short C-C bonds of the cyclo[18]carbon are evidently stronger than benzene and even comparable to ethene.

Above analyses suggest that the extent of global electron delocalization of the cyclo[18]carbon can neither be underestimated nor overestimated.

Aromaticity and response to external magnetic field

Due to the global electron delocalization nature in the cyclo[18]carbon and the fact that the number of its π electrons satisfies the Hückel's $4n+2$ rule, it is naturally expected that this system should exhibit significant aromaticity and the π electrons can form unidirectional induced current when external magnetic field is applied. In this section we will investigate these points.

Multicenter bond order is a very reliable and useful method in measuring multi-center

conjugation and aromaticity.^[60] Unfortunately, its calculation is computationally prohibitively high for large rings, such as the case of cyclo[18]carbon. Recently AV1245 was proposed,^[61] it can give similar result to multi-center bond order while can be easily applied to a ring consisting of dozens of atoms. The AV1245 for the cyclo[18]carbon was computed to be 4.25, which is a fairly large value, rendering that this system shows remarkable aromaticity. It is also worth to mention that the AV1245 of the 18-membered carbon ring in the 18-annulene ($C_{18}H_{18}$) is only 2.40, indicating that its overall aromaticity is by far weaker than the cyclo[18]carbon.

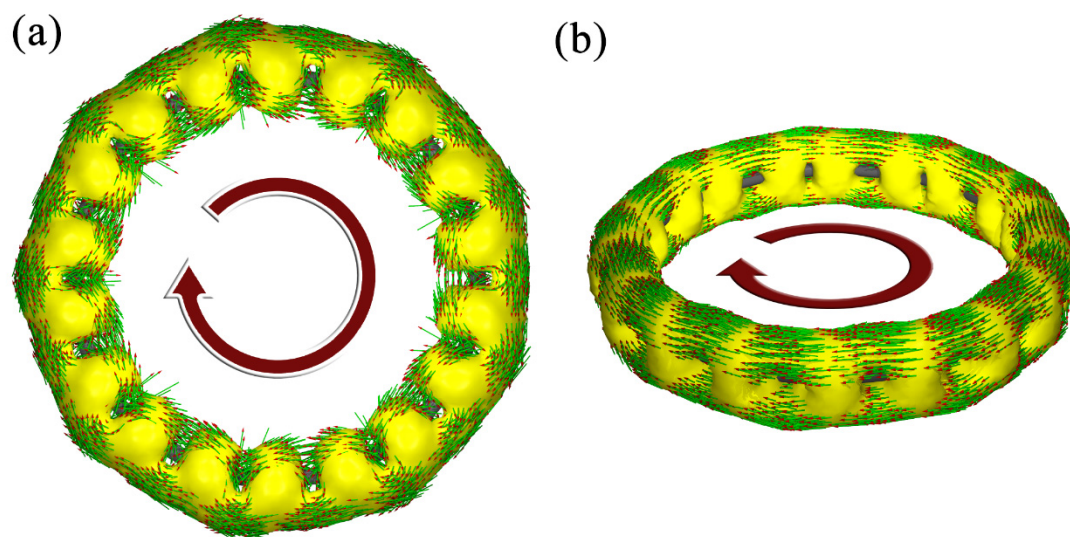


Fig. 9 Induced ring current of cyclo[18]carbon calculated by ACID method. The green arrows represent direction and magnitude of the current at various positions on the ACID isosurface of 0.05. For clarity, very small arrows are removed. (a) and (b) exhibit the ring current formed by in-plane and out-plane π electrons, respectively. In (a), the direction of the applied magnetic field is outward along the screen, while in (b) the direction is from bottom to top.

The anisotropy of the current-induced density (ACID)^[17] is a very popular method in graphically revealing induced ring current under external magnetic field, and it can be decomposed as contributions of different MOs. Figs. 9(a) and 9(b) present the ring current contributed by in-plane and out-plane π electrons, respectively. In both maps the ring current is strong and fully obeys the left-hand rule, this observation provides strong evidence that the cyclo[18]carbon possesses double aromaticity. It is worth to note that in Fig. 9(a) the unidirectional ring current corresponding to the in-plane π electrons formed at both inner side and outer side of the ring, this interesting phenomenon is extremely rare.

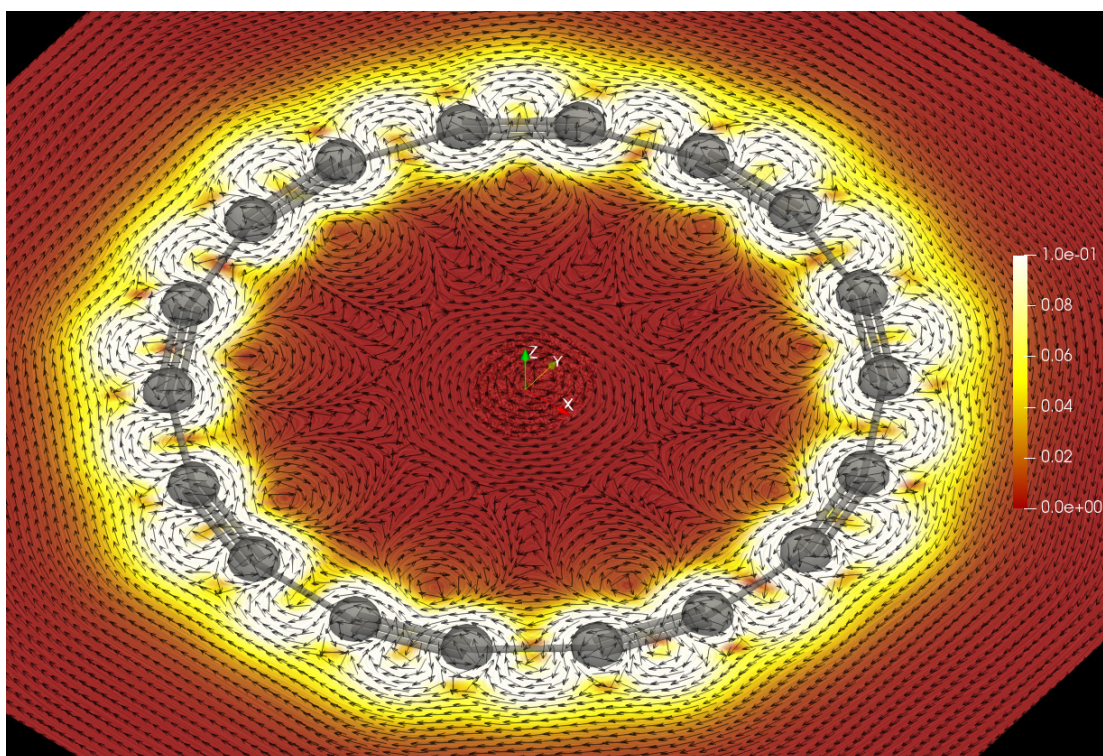


Fig. 10 GIMIC map in the molecular plane of cyclo[18]carbon. The arrows indicate direction of induced current, the color correspond to magnitude of induced current. The applied magnetic field is along positive direction of Z-axis.

The gauge-including magnetically induced currents (GIMIC) is an alternative method of exhibiting the current induced by external magnetic field.^[62] The GIMIC map in the molecular plane of the cyclo[18]carbon is shown as Fig. 10, which provides a complementary perspective to the ACID map. The Fig. 10 vividly shows that significant diatropic current formed in both inner and outer edges of the ring. The diatropic current refers to the induced current whose direction satisfies left-hand rule. From the GIMIC map we can draw the same conclusion as ACID map that cyclo[18]carbon has strong aromatic characteristics. In the supplemental material, we provided an animation file rendered by ParaView visualization program^[63] based on the vector field of current ring generated by the GIMIC code to intuitively show dynamic character of the ring current, we highly recommend interested reader to watch it.

An advantage of the GIMIC code is that strength of current passing a given plane can be obtained by numerical integration of current flow, this allows us to quantitatively examine aromaticity in terms of induced current. The calculated current strength passing through the normal plane placed at the midpoint of the short C-C bonds is 25.8 nA/T, while the value for the long C-C bonds is slightly lower, namely 24.7 nA/T. For comparison purpose, we also calculated the integrated induced current for C-C bonds of benzene, the result 12.2 nA/T is much smaller than that of the bonds in the cyclo[18]carbon, displaying cyclo[18]carbon has huge overall aromaticity.

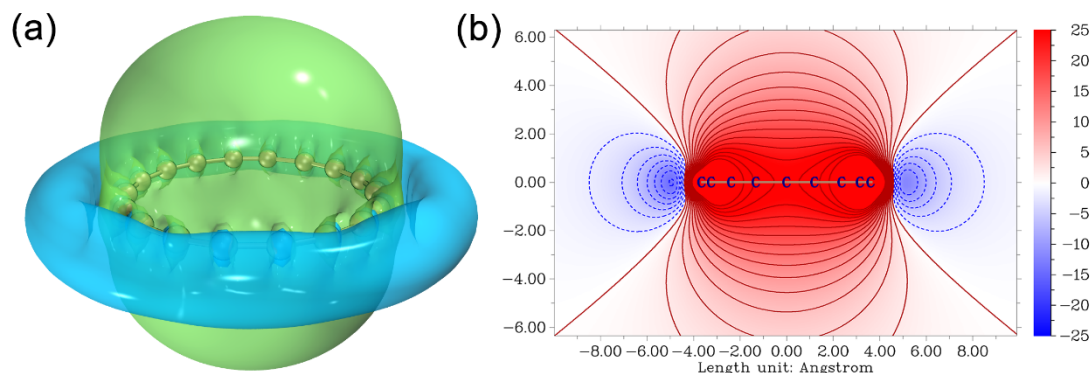


Fig. 11 ZZ component of iso-chemical shielding surface (ICSS_{ZZ}) of cyclo[18]carbon. (a) Isosurface map. Green and blue correspond to $\text{ICSS}_{\text{ZZ}}=7.0$ (shielding) and -7.0 ppm (deshielding), respectively. (b) Contour line map of ICSS_{ZZ} in the slice plane perpendicular to the ring.

The iso-chemical shielding surface (ICSS)^[56,64] is a method closely related to the well-known nucleus-independent chemical shifts (NICS).^[65] NICS studies chemical shielding against external magnetic field at specific points, while ICSS extends the idea of NICS to the whole space, it calculates magnetic shielding tensor at every evenly distributed grid point around the system and then plots certain component of the tensors as isosurface map. The isosurface map of ZZ component of ICSS (ICSS_{ZZ}) of the cyclo[18]carbon is presented as Fig. 11(a). The ICSS_{ZZ} is a real space function that able to clearly exhibits extent of shielding or deshielding effect on external magnetic field in the direction perpendicular to the ring. From Fig. 11(a) it can be seen that in the ring center area as well as the regions above and below the ring, the shielding effect is quite prominent. In addition, there is a circular region showing deshielding effect around the ring. This ICSS_{ZZ} distribution character is very akin to the case of benzene, which is a prototype aromatic system, hence the ICSS_{ZZ} analysis further demonstrated that cyclo[18]carbon has conspicuous aromaticity.

The ICSS_{ZZ} can be examined more clearly from Fig. 11(b), which represents ICSS_{ZZ} in the slice plane perpendicular to the ring. From this map one can find that the magnetic shielding effect is fairly large and varies very smoothly in the inner region of the ring. The ICSS_{ZZ} value at the ring center (*i.e.* $\text{ICSS}_{\text{ZZ}}(0)$) and at the point above $1 \text{ \AA}$ of the ring center (*i.e.* $\text{ICSS}_{\text{ZZ}}(1)$) is 25.7 and 23.7 ppm, respectively, while the corresponding values of benzene at the same calculation level are 16.1 and 29.9 ppm. The relatively larger $\text{ICSS}_{\text{ZZ}}(1)$ of benzene implies that benzene has stronger π aromaticity than the out-plane π aromaticity of the cyclo[18]carbon, while the relatively larger $\text{ICSS}_{\text{ZZ}}(0)$ of the cyclo[18]carbon should result from its unique in-plane π aromaticity, which is missing in benzene.

Molecular electrostatic potential

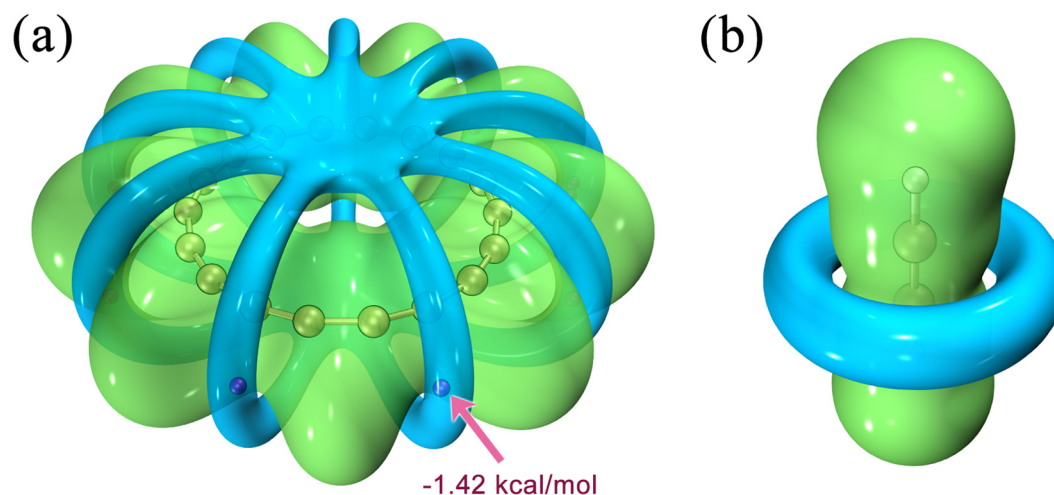


Fig. 12 Isosurface map of electrostatic potential (ESP). (a) Cyclo[18]carbon. Green and blue isosurfaces correspond to $\text{ESP} = 0.001$ and -0.001 a.u. (6.28 and -6.28 kcal/mol), respectively. Minima of ESP are plotted as purple spheres. (b) Acetylene. Green and blue isosurfaces correspond to $\text{ESP} = 0.02$ and -0.02 a.u., respectively. The ESP at its minimum is -20.03 kcal/mol.

Electrostatic potential (ESP)^[66,67] measures interaction energy between a unit charge at a given point and the present system without charge transfer and charge polarization effects, it is interplayed by both nuclear charges and electronic charges. Since ESP plays a crucial role in determining electrostatically dominated weak interaction between a system and other substances, while weak interaction is a quite important aspect of the cyclo[18]carbon, we calculated and plotted isosurface of ESP for this system under a properly selected isovalue, see Fig. 12(a). The ESP distribution of the cyclo[18]carbon is quite interesting, it can be seen that most molecular regions have positive ESP, the value is slightly negative only in the circular area surrounding each of the short C-C bonds as well as in the regions above and below the ring center. This unique shape of negative ESP regions remind us of the ESP isosurface of acetylene, see Fig. 12(b). As can be seen, the acetylene also has a circular negative ESP isosurface around its C-C triple bond, however its ESP minimum (-20.03 kcal/mol) is much more negative than that of cyclo[18]carbon (-1.42 kcal/mol). This comparison suggests that the negative ESP region of the cyclo[18]carbon should originate from the fact that its short C-C bonds have double π interactions like acetylene; however, as the strength of its π interaction is evidently weaker than acetylene, leading to relatively less electron aggregation around the bonding region, the minimum of ESP near the bond is not so negative as acetylene.

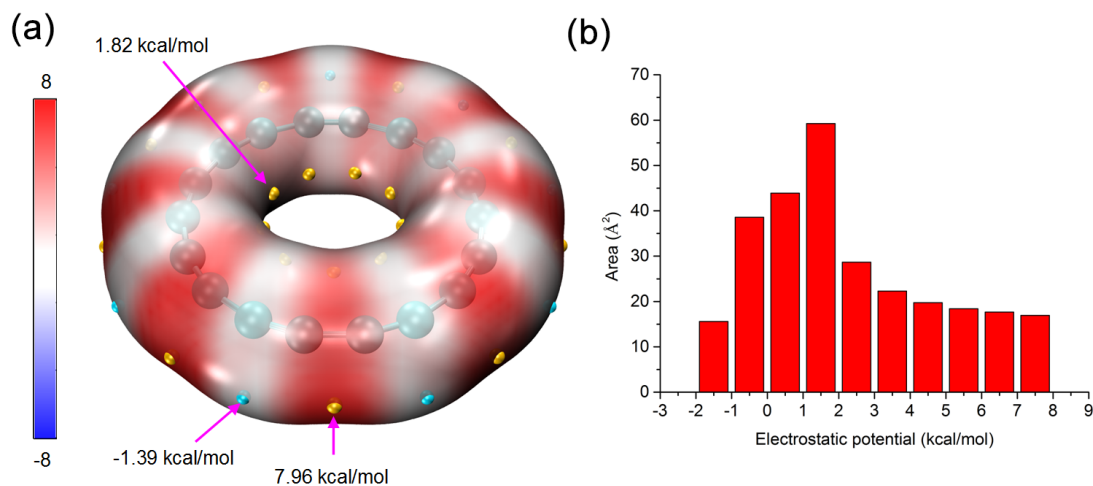


Fig. 13 (a) Electrostatic potential (ESP) mapped van der Waals surface (*i.e.* $\rho = 0.001$ a.u. isosurface) of cyclo[18]carbon. The redder the color, the more positive the ESP. Minima and maxima of ESP on the surface are drawn as cyan and orange spheres, respectively. (b) Area distribution of different ESP intervals.

ESP on vdW surface is often investigated because it is very closely related to intermolecular electrostatic interactions.^[68-71] In order to predict possible interactions that driven by electrostatics effect between the cyclo[18]carbon and other chemical substances, we performed quantitative molecular surface analysis^[72] to locate ESP maxima and minima on the vdW surface, as shown in the Fig. 13(a). The ESP colored vdW surface map is also simultaneously given. In addition, we calculated area distribution of different ESP intervals on the vdW surface^[73,74] and plotted it as Fig. 13(b). From the maps we can find two interesting points:

First, from the labelled texts in Fig. 13(a) it can be seen that the ESP on the vdW surface ranges from -1.39 to 7.96 kcal/mol, which is a relatively narrow range, indicating that the cyclo[18]carbon is incapable of forming strong electrostatic interaction to other molecules. Relatively speaking, the cyclo[18]carbon more tends to act as a Lewis acid to bound Lewis base species, not only because on the vdW surface the magnitude of ESP at maxima is larger than that at minima, but also because the surface area with positive ESP is much larger than that with negative ESP, as can be clearly observed from Fig. 13(b).

Second, from distribution of the surface ESP extrema in Fig. 13(a) one can see that positive ESP only occurs on the local vdW surface surrounding the long C-C bonds, while around the short C-C bonds the surface only shows weakly negative ESP, this phenomenon is closely related to the ESP spatial distribution shown in Fig. 12(a). The nature of the uneven distribution of ESP on the vdW surface should essentially result from the unequal amount of π electrons on the different kinds of C-C bonds.

Previously we defined an index named molecular polarity index (MPI) for quantitatively measuring polarity of molecules based on ESP on their vdW surfaces, it is expressed as

$$\text{MPI} = (1/A) \iint_S |V(\mathbf{r})| dS$$

where the A is area of vdW surface, the S denotes the integration is performed over molecular surface, $V(\mathbf{r})$ stands for ESP. The MPI of the cyclo[18]carbon is found to be 2.60 kcal/mol, while at the same

calculation level the MPI of ethane, ethene and benzene are 2.62, 6.70 and 8.45 kcal/mol, respectively. Clearly the polarity of the cyclo[18]carbon is quite low, as its MPI value is close to saturated hydrocarbons, which are usually viewed as fully nonpolar molecules. Note that according to the MPI, even the unsaturated hydrocarbons such as ethene and benzene have higher polarity than the cyclo[18]carbon.

Dimer structure and π - π interaction

Compared with the countless complexes formed by the cyclo[18]carbon and other molecules, the dimer formed between the cyclo[18]carbon and itself is more worth to research, because this model is important in understanding the actual status of the cyclo[18]carbon in condensed phase. Given that cyclo[18]carbon has fully planar structure, large amount of π electrons over the ring and very low polarity, it is expected two cyclo[18]carbon can form a dimer bounded by strong π - π interaction.

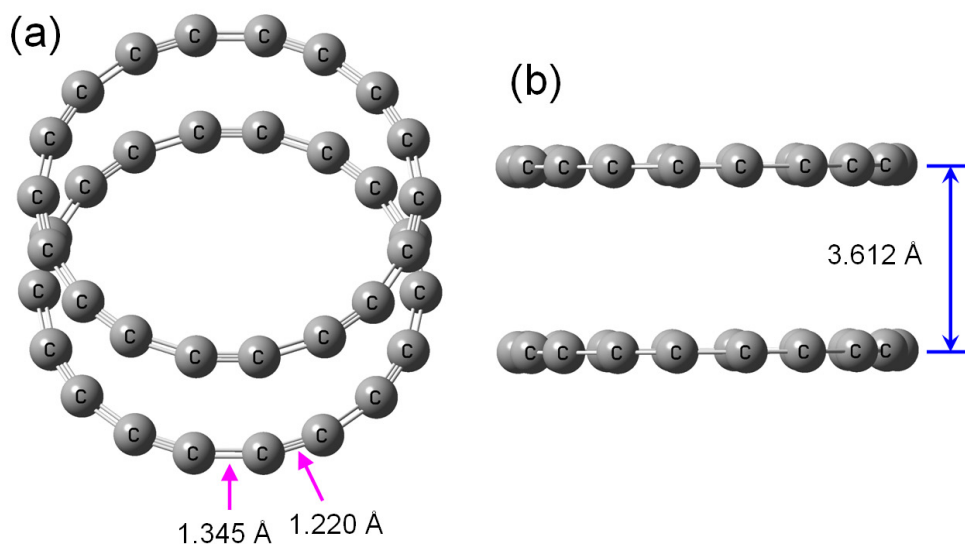


Fig. 14 Structure of optimized cyclo[18]carbon dimer. No imaginary frequency can be found. (a) Oblique view (b) Side view.

The cyclo[18]carbon dimer was optimized by us at ω B97XD/def2-TZVP level, see Fig. 14 for illustration. The geometry is found to have D_{9d} point group, the two rings parallelly stacked together in exact face-to-face manner, the spacing between the two rings is 3.612 Å. Note that as can be seen from Fig. 14, in this dimer each short C-C bond in one ring faces a long C-C bond in another ring, this should be the consequence of ESP complementation principle (recall the Fig. 12(a) that the ESP is positive and negative around the local vdW surface corresponding to the long and short C-C bonds, respectively). Since the stacking belongs to weak interaction, the bond lengths are not detectably affected, it is found that length variation of the short and long C-C bonds during the dimerization is merely 0.0010 and -0.0007 Å, respectively.

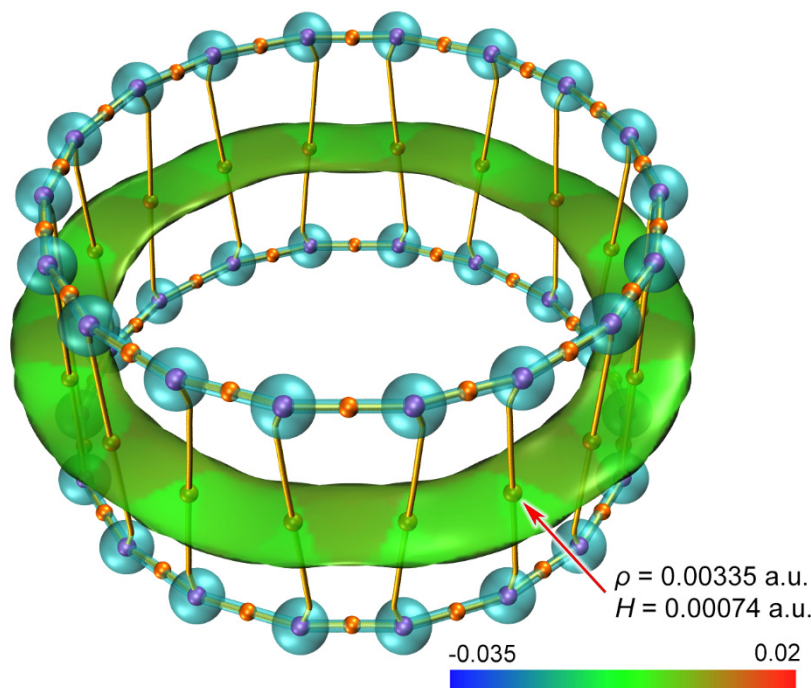


Fig. 15 Interaction between two cyclo[18]carbon monomers in the optimized dimer structure. Nuclear critical points and bond critical points are shown as purple and orange spheres, respectively. Bond paths are drawn as yellow paths. Molecular structure is represented as cyan transparent CPK model. The green circular region between the two rings is isosurface of reduced density gradient (RDG) of 0.8 mapped by $\text{sign}(\lambda_2)\rho$ function. The electron density (ρ) and energy density (H) at a BCP between the two rings are labelled.

The AIM^[52,68-70,75] and non-covalent interaction (NCI)^[14,76] are both very useful and popular analysis methods for investigating weak interactions. The former mainly studies the interactions in a quantitative manner based on the properties at the corresponding BCPs, while the latter focuses on visually revealing the interaction regions and interaction types. The two methods provide complementary perspectives to weak interactions. The BCPs and accompanied bond paths calculated for the cyclo[18]carbon dimer are shown in Fig. 15, representative interaction paths between the two rings are displayed as orange paths, there is a BCP at approximately midpoint of each path. The positive energy density at the BCPs suggests that the interaction between the two rings should be regarded as closed-shell interaction,^[77] while the very low electron density at the BCPs manifests that the strength of each interatomic pairwise interaction is quite weak.

The NCI map, namely the $\text{sign}(\lambda_2)\rho$ mapped reduced density gradient (RDG) isosurface, is also plotted in Fig.15. The colored RDG isosurface provides a much more intuitive picture about the interaction than the AIM topology map. It can be seen that there is a very broad and flat circular isosurface sandwiched between the two rings, which clearly portrays the major interaction region corresponding to the π - π stacking. Because of the very large π - π contact between the two rings, as vividly revealed by the NCI map, it is expected that the interaction strength between the two cyclo[18]carbon monomers should be large, at least greater than most of π - π stacking interactions formed between small aromatic molecules.

Table 3 Interaction components between the two cyclo[18]carbon monomers in the dimer calculated by scaled SAPT0/jun-cc-pVDZ

Component	Value (kJ/mol) ^a
Exchange	51.8
Electrostatics	-22.4 (19.2 %)
Induction	-5.7 (4.9%)
Dispersion	-88.6 (76.0 %)
Total interaction	-64.7

^a The values in the parentheses correspond to percentage contributions of various terms to total attractive interaction, which is defined as sum of electrostatics, induction and dispersion in the present context.

In order to elucidate the π - π stacking interaction between the cyclo[18]carbons from an energy perspective, we conducted symmetry-adapted perturbation theory (SAPT) analysis.^[75,78,79] This method can not only present total interaction energy, but can also give individual physical components to better understand the interaction nature. Scaled SAPT0/jun-cc-pVDZ level was employed in our analysis. Ref. [78] demonstrated that the mean absolute errors of this level in estimating interaction energy is merely 0.49 kcal/mol, which is satisfactory. As also indicated in ref. [78], using the higher level SAPT2+/aug-cc-pVDZ should result in better accuracy, however it is not computationally affordable for the present dimer. The calculated physical components of the interaction energy are listed in Table 3. It can be seen that the estimated total interaction energy is -64.7 kJ/mol, which is approximately as large as three times of binding energy of the hydrogen-bond in a water dimer, therefore it is expected that the double ring structure of the cyclo[18]carbon dimer should be stable in real environment when temperature is not high. Table 3 also shows that the major nature of the attractive interaction between the two monomers is dispersion, which is known as the true essence of π - π stacking,^[80] thus now we can consolidate our conclusion that the two monomers in the dimer are binded by typical π - π stacking effect. Furthermore, Table 3 exhibits that electrostatics component only plays a minor role in the attractive interaction, while the induction effect is even fully negligible, this is also a commonly observed feature in π - π stacked dimers. The low electrostatics component should be the direct consequence of the very low ESP distribution over the vdW surface of the cyclo[18]carbon.

It is worth noting that although the scaled SAPT0 analysis is able to provide useful insight into the interaction for the cyclo[18]carbon dimer, due to the particularity of the electronic structure of the cyclo[18]carbon, the absolute interaction energy estimated at this level may be not quite reliable. Therefore, we also calculated the interaction energy via two other levels, namely ω B97XD in combination with ma-TZVP^[81] basis set plus Counterpoise correction,^[82] as well as ω B97M-V^[83] in conjunction with def2-QZVPP basis set^[11], the former and the latter calculations were finished by Gaussian 16 and ORCA 4.2.1, respectively. The interaction energies yielded by these two levels are very similar, namely -35.1 and -35.8 kJ/mol, respectively. We believe that they should be more close to the exact solution than the -64.7 kJ/mol provided by the scaled SAPT0/jun-cc-pVDZ calculation, since we already know that ω B97XD is able to nicely describe the cyclo[18]carbon and it is well known that ω B97XD can give reasonable weak interaction energies^[24]; in addition, ref. [84] demonstrated that the ω B97M-V is currently the best DFT functional for evaluating non-covalent interactions.

Reactivity

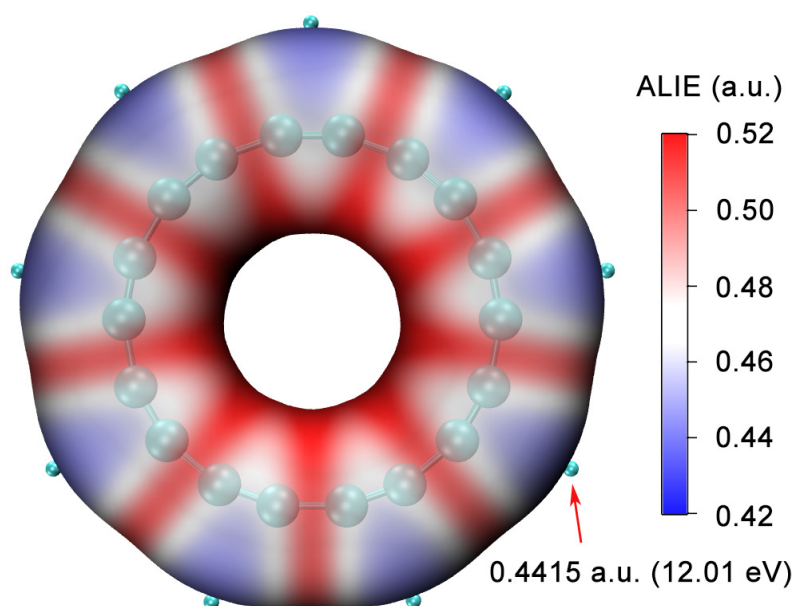


Fig. 16 Average local ionization energy (ALIE) mapped van der Waals surface (*i.e.* $\rho = 0.001$ a.u. isosurface) of cyclo[18]carbon. Cyan spheres indicate position of minima of ALIE on this surface.

Reactivity of the cyclo[18]carbon is quite worth to explore due to its unusual electronic structure. There are large number of analysis methods that can be used to predict preferential reactive sites and reveal capacity of participating in chemical reactions.^[85,86] Here we employ the average local ionization energy (ALIE)^[38,87,88] to study the cyclo[18]carbon. The ALIE is a real space function reflecting ionization energy of an electron in a local region. At a given position, the lower the ALIE, the weaker the electrons are bound, and the higher the reactivity of the electrons. The ALIE mapped molecular vdW surface is shown in Fig. 16, the ALIE minima on the surface are highlighted as cyan spheres. According to the mapped color in this figure it can be seen that around the long C-C bonds, the ALIE is large and thus the electrons are relatively tightly bounded at that places, while the most active electrons are distributed at the outer surface over the short C-C bonds. Recall that in these regions the ESP is slightly negative, it is expected that the short C-C bonds in the cyclo[18]carbon can be relatively easily attacked by electrophiles and participate in electrophilic reactions, at least compared to the long C-C bonds. As a comparison, the lowest ALIE value on vdW surface of some other molecules containing π electrons are given here: benzene (11.06 eV), ethene (10.45 eV), acetylene (11.17 eV). The corresponding value of the cyclo[18]carbon (12.01 eV) is larger than them to different extents, implying that cyclo[18]carbon may has relatively higher chemical stability to electrophiles.

UV-Vis spectrum and electronic excited states

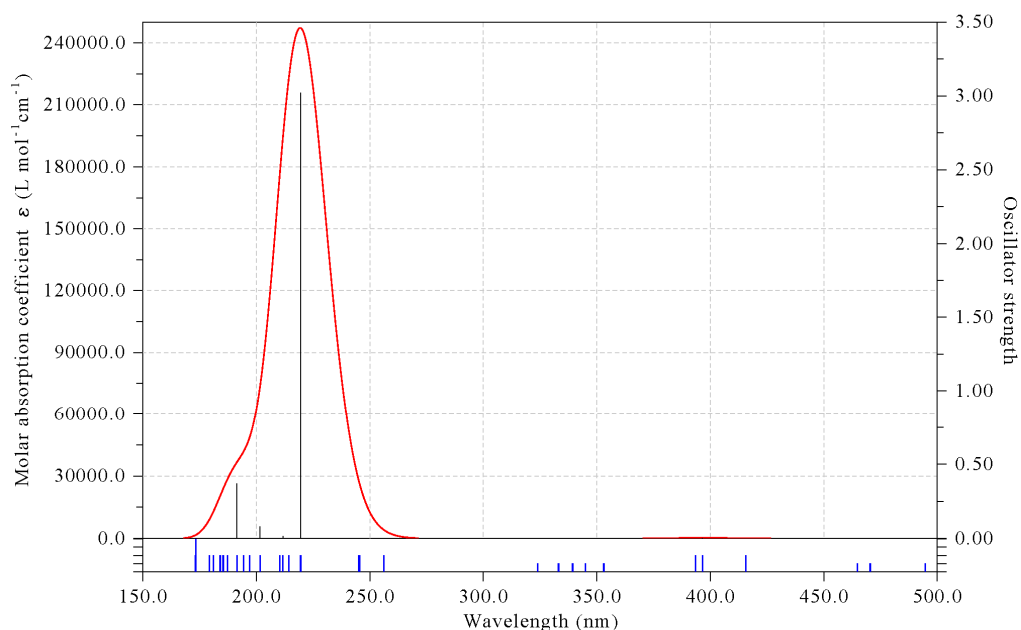


Fig. 17 Simulated UV-Vis spectrum of cyclo[18]carbon. The red curve corresponds to molar absorption coefficient broadened by calculated excitation energies and oscillator strengths, the latter are shown as black spikes. The blue spikes are used to highlight positions and degeneracy of the excitations, neighbouring excitations are regarded as degenerate if their energy difference is less than 0.005 eV.

Electronic absorption spectrum is an important feature of a molecule. We employed time-dependent DFT (TDDFT) theory at $\omega\text{B97XD/def2-TZVP}$ level to calculate the first 50 excited states. The resulting data was used to simulate UV-Vis spectrum by Gaussian broadening function with full width at half maximum (FWHM) of 2/3 eV, see Fig. 17. It can be seen that there is an extremely strong absorption band, its peak at 219.5 nm sources from doubly degenerate $S_0 \rightarrow S_{21}$ and $S_0 \rightarrow S_{22}$ excitations, whose oscillator strengths reach as high as 3.02. The second strongest absorption corresponds to the doubly degenerate $S_0 \rightarrow S_{35}$ and $S_0 \rightarrow S_{36}$ at 191.5 nm. All other excitations do not have detectable contributions to the UV-Vis spectrum because their oscillator strengths are negligible or exactly zero due to symmetry forbidden. Since there is no evident absorption band in the visible region (380~760 nm), the pure cyclo[18]carbon is expected to be colorless.

It is worth to note all the calculated 50 excited states correspond to pure $\pi\text{-}\pi^*$ transitions, neither $\sigma\text{-}\pi^*$ nor $\pi\text{-}\sigma^*$ composition is detected since the excitation energy for this type of transition must be very high. According to the type of MOs, there are four kinds of MO transitions involved in the electronic excitations, namely in-plane π MO to in-plane π^* MO, in-plane π MO to out-plane π^* MO, out-plane π MO to in-plane π^* MO, and out-plane π MO to out-plane π^* MO. An examination of configuration coefficients shows that many excitations exhibit mixed type of transitions. For example, as shown in Fig. 18, the $S_0 \rightarrow S_{21}$ excitation shows nearly half and half in-plane $\pi\text{-}\pi^*$ transition and out-plane $\pi\text{-}\pi^*$ transition.

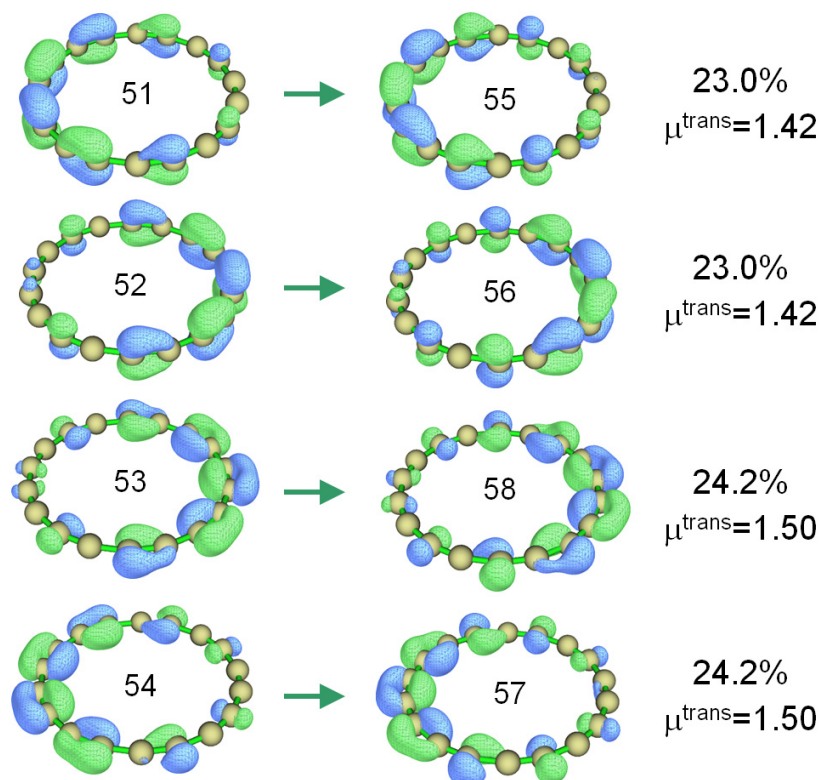


Fig. 18 Dominant contributions of MO transitions to the $S_0 \rightarrow S_{21}$ excitation of cyclo[18]carbon. Contributions from these major MO transitions to the transition dipole moment are shown as μ^{trans} (in a.u.). The labelled indices correspond to the MO indices sorted by energy from low to high. The isosurfaces exhibit MO wavefunctions, green and blue parts correspond to isovalues of 0.05 and -0.05, respectively.

Why the oscillator strength of $S_0 \rightarrow S_{21}$ and $S_0 \rightarrow S_{22}$ is so large? In order to provide an insight into this question, given that oscillator strength is proportional to square of magnitude of transition dipole moment (μ^{trans}), we decomposed the μ^{trans} of $S_0 \rightarrow S_{21}$ as contributions from different MO transitions, the values of the four dominant ones are labelled in Fig. 18. It can be seen that the four major MO transitions have nearly the same contributions to μ^{trans} , in each transition the occupied MO (hole orbital) and unoccupied MO (electron orbital) occupy basically the same spatial region. Because significant overlap of hole and electron distributions is a precondition of large transition dipole moment, it is naturally expected that the $S_0 \rightarrow S_{21}$ should have large μ^{trans} .

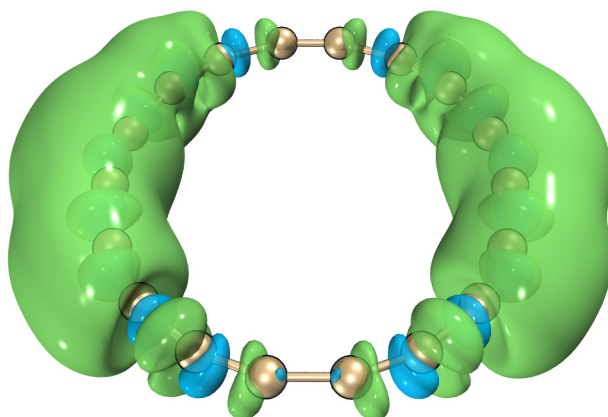


Fig. 19 X component of transition dipole moment density of S0→S21 of cyclo[18]carbon. The X direction corresponds to the transition dipole moment vector. The isovalue is set to 0.003, the green and blue correspond to positive and negative parts, respectively.

The very large μ^{trans} of S0→S21 of cyclo[18]carbon can also be studied in terms of transition dipole moment density, which is a real space function exhibiting contribution of every spatial position to transition dipole moment.^[89] The corresponding isosurface map is given in Fig. 19. It can be seen that the electron distribution at the left side and right side of the map has huge contribution to the μ^{trans} since there are considerably large green isosurfaces. From the expression of transition dipole moment density it is easy to understand that the occurrence of these two regions is direct consequence of the very prominent overlap between the hole and electron orbitals in that places.

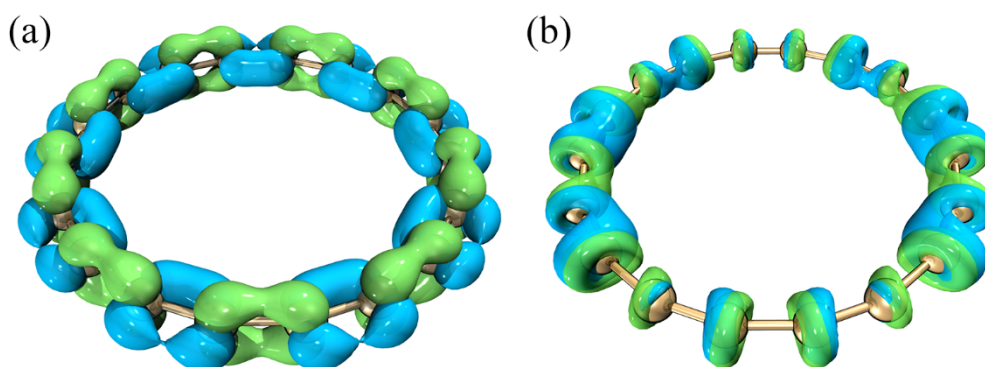


Fig. 20 Real space representation of hole and electron distributions for (a) S0→S1 excitation and (b) S0→S21 excitation. Green and blue isosurfaces correspond to electron and hole distributions, respectively. Isovalue is set to 0.003.

The hole-electron analysis developed by us is a very useful and powerful method in unraveling nature of electron excitations^[89] and has been employed by quite a few research articles.^[90-92] In many cases, the electronic excitation cannot be well represented by only one pair of MO transition, bringing great difficulty in examining its characteristics. This difficulty is completely resolved in our hole-electron analysis. For any excitation, this theory is able to present a unique distribution of hole and electron, the former describes where the excited electron leaves, and the latter describes

where the excited electron goes. We applied the hole-electron analysis to not only the aforementioned important $S_0 \rightarrow S_{21}$ excitation, but also to the $S_0 \rightarrow S_1$ excitation, because according to the Kasha's rule the S_1 is commonly the excited state to emit fluorescence and thus plays a vital role in molecular photophysics. From the Fig. 20 (a), one can directly infer that during the $S_0 \rightarrow S_1$ excitation, the excited electron leaves the in-plane occupied π orbitals that correspond to the short C-C bonds and goes to the unoccupied orbitals which represent anti- π interaction on the long C-C bonds. Therefore, it is expected that in the S_1 state the long and short C-C bonds become stronger and weaker compared to the S_0 state, respectively; as a consequence, the properties of the two kinds of bonds should tend to be equalized. The Fig. 20(b) shows that the $S_0 \rightarrow S_{21}$ excitation is more involved than the $S_0 \rightarrow S_1$, since its hole and electron are not evenly distributed on the ring, but concentrated on the two sides of the system and highly overlap with each other. In addition, from the shape of the hole and electron it can be anticipated that the excitation shows mixed character, namely both in-plane and out-plane π MOs are simultaneously involved, because the nodal plane character of the hole and electron is neither similar to the in-plane π MOs nor to the out-plane π MOs.

Molecular vibrations as well as IR and Raman spectra

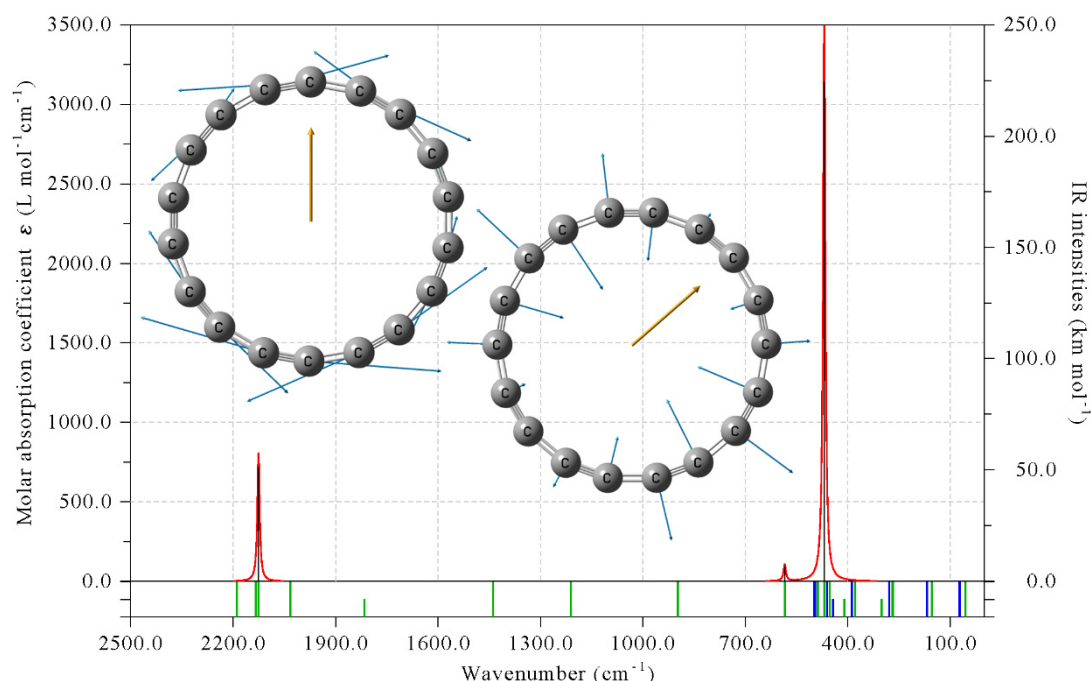


Fig. 21 Simulated infrared (IR) spectrum of cyclo[18]carbon. The red curve corresponds to molar absorption coefficient, while the black spikes correspond to theoretically calculated IR intensities. The green and blue spikes at bottom of the map indicate frequencies of in-plane and out-of-plane vibrational modes, respectively. The atomic motion corresponding to the two most active modes is illustrated as insets, the yellow arrows represent direction of derivative vector of dipole moment with respect to canonical vibrational coordinate.

In Fig. 21, simulated infrared (IR) spectrum is presented in order to help experimental chemists to judge the existence of this system by comparing the spectra. The harmonic frequencies

calculated at ω B97XD/def2-TZVP were scaled by 0.95 to approximately eliminate systematical error due to the harmonic approximation.^[93] The current system has two kinds of vibrations, namely in-plane and out-of-plane vibrations, they are highlighted as green and blue spikes in the Fig. 21, respectively. There are several worth noting observations from the figure:

(1) The in-plane vibration modes span the whole spectral range, while the out-of-plane modes only concentrate in low wavenumber region. This phenomenon indicates that all out-of-plane vibrations in this system correspond to flexible motion.

(2) Many vibrational modes are doubly degenerate due to point group symmetry.

(3) Most majority of the vibrations are forbidden transitions, namely the corresponding IR intensities are exactly zero. This is because the cyclo[18]carbon has high order point group symmetry, resulting in vanished transition dipole moments between vibrational ground state and first vibrational excited state for many modes.

(4) There are only two relatively intensive IR peaks, the corresponding vibrational coordinates are shown as insets of the Fig. 21. The first one is at 2125.1 cm^{-1} and mainly corresponds to stretching motion of some short C-C bonds, while the second one is at 469.1 cm^{-1} and corresponds to in-plane alternate bending of some bond angles. It is well known that significant change in molecular dipole moment during vibration is a precondition of large IR intensity, in order to better understand why the two aforementioned vibrations have notable IR intensities, the derivative vectors of molecular dipole moment with respect to their vibrational coordinates are plotted as orange arrows in the insets of Fig. 21, which clearly exhibit directional change of molecular dipole moment during the vibrations.

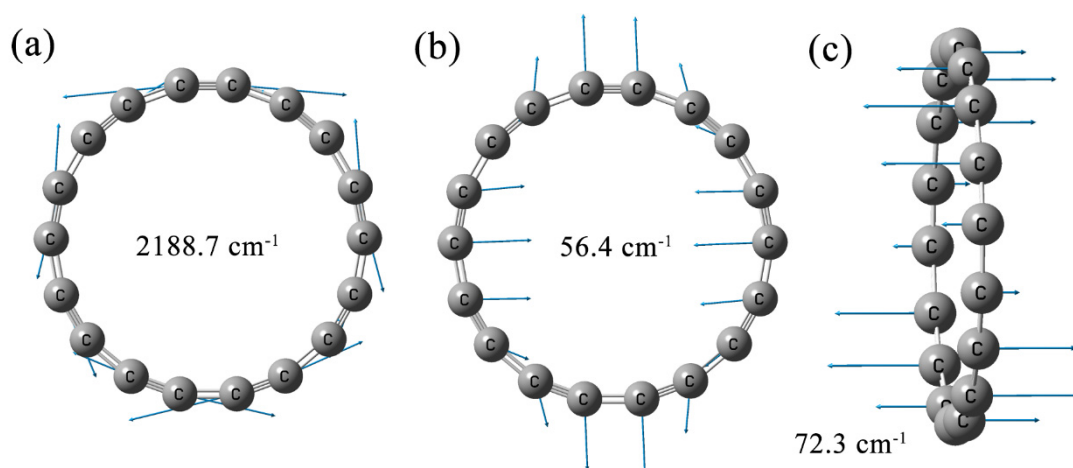


Fig. 22 Three featured vibrational modes of cyclo[18]carbon. (a) Highest vibrational mode (b) Lowest in-plane vibrational mode (c) Lowest out-of-plane vibrational mode.

In order to better exhibit vibrational character of the cyclo[18]carbon, its three featured vibrational modes are plotted as Fig. 22. It can be seen that the mode with highest wavenumber is at 2188.7 cm^{-1} and shows C-C stretching motion, the large wavenumber implies large force constant and strong rigidity of the bonds. The lowest in-plane vibrational mode corresponds to deformation motion varying from circle to ellipse, its very low wavenumber (56.4 cm^{-1}) exhibits that PES along this and similar modes is quite floppy. The rather small wavenumber (72.3 cm^{-1}) of the lowest out-of-plane mode suggests that in the out-of-plane direction the ring is extremely flexible.

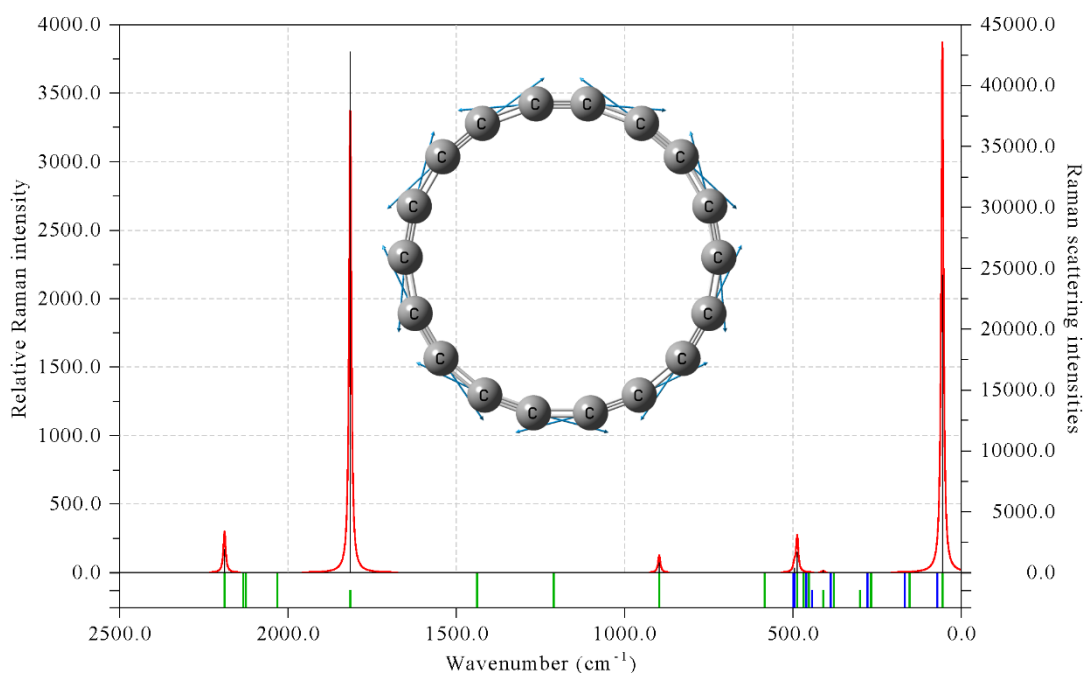


Fig. 23 Simulated Raman spectrum of cyclo[18]carbon with incident light at wavelength of 1064 nm. The red curve was broadened from calculated Raman intensities, which are represented as black spikes. The green and blue spikes at bottom of the map indicate frequencies of in-plane and out-of-plane vibrational modes, respectively. The atomic motion corresponding to the mode with strong Raman intensity at 1815.2 cm^{-1} is exhibited in the inset.

We also simulated Raman spectrum for the cyclo[18]carbon at the same calculation level as IR spectrum, see Fig. 23. Note that the Raman intensities needed by theoretical simulation of Raman spectrum cannot be directly outputted by Gaussian, therefore they were converted from the Raman activities printed by Gaussian with temperature of 298.15 K and incident light of 1064 nm via the formula described in ref. [94]. The 1064 nm wavelength corresponds to the common Raman source Nd:YAG laser. The Fig. 23 shows that there are two strong Raman peaks, which are respectively at a high wavenumber 1815.2 cm^{-1} and a very low wavenumber 56.4 cm^{-1} . The former one corresponds to bond stretching mode, as shown in the inset of Fig. 23, while the latter one corresponds to in-plane ring deformation, as shown in Fig. 22(b). It can be seen that the IR spectrum and Raman spectrum of the cyclo[18]carbon show evident complementary feature to each other. There are also many modes show neither IR nor Raman intensities, hence they cannot be captured by any common experimental measure.

Molecular dynamics

The dynamics behavior of the cyclo[18]carbon is quite worth to explore. According to the calculated vibration frequencies it can be inferred that the cyclo[18]carbon can hardly maintain the D_{9h} structure in real environment due to the thermal motion of the atoms, because it possesses a large number of flexible vibration modes. In order to investigate geometry fluctuation and thermal stability of the cyclo[18]carbon, we carried out *ab-initio* molecular dynamics simulation at ω B97X-

D3/def-TZVP level for this system in vacuum. Totally three 2000 fs trajectories were respectively simulated at 100, 200 and 298.15 K. From Fig. S5 it can be seen that the actual average temperatures are very close to the corresponding reference temperatures, showing that the temperatures were well maintained by the thermostat. The geometry optimized under ω B97XD/def2-TZVP level was employed as the initial coordinate, the atomic velocities were initialized according to Maxwell-Boltzmann at corresponding simulation temperatures.

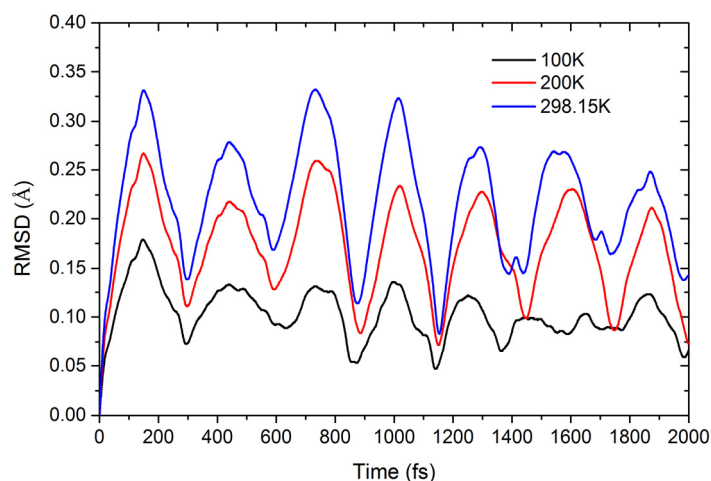


Fig. 24 Root mean square deviation (RMSD) of three *ab-initio* molecular dynamics trajectories simulated at different temperatures of cyclo[18]carbon with respect to its optimized structure, which corresponds to the first frame of the trajectories. The frames in the trajectories have been aligned to the first frame prior to the calculation of the RMSD.

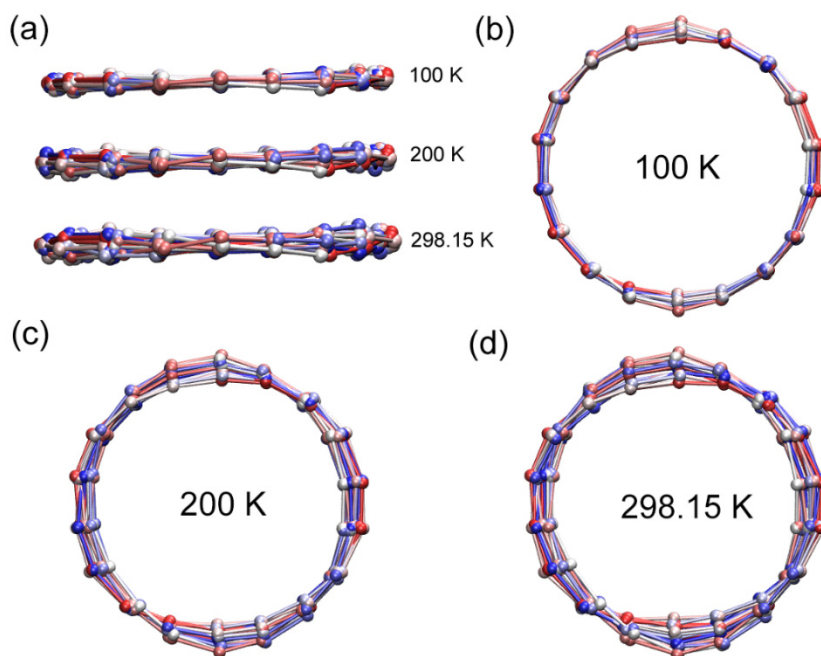


Fig. 25 Structure variation of cyclo[18]carbon during the 2000 fs trajectories simulated at different temperatures. (a) Side views. (b), (c), (d) Vertical views. The structures are drawn every 100 fs, the color corresponds to time step and varies as red-white-blue.

Isomerization and dissociation were not observed during the 2000 fs simulation for the cyclo[18]carbon at any temperature. The RMSD curves of the three simulated trajectories are shown in Fig. 24, from which we can find that the overall structure of this system shows regular fluctuation, especially at the relatively high temperatures (200 and 298.15 K). The fluctuation period is found to be approximately 300 fs, which corresponds to frequency of 3.3 THz or 111 cm^{-1} . The curves exhibit that the higher the simulation temperature, the larger the geometry fluctuation. This can be more clearly recognized from Fig. 25, which presents structures of the cyclo[18]carbon extracted every 100 fs from the trajectories. It can be seen that at 298.15 K, the cyclo[18]carbon undergoes both considerable in-plane and out-of-plane geometry distortions, while the extent of the distortions is insignificant at 100 K. We also provided the animation file corresponding to the simulation at 298.15 K in supplemental material, from which the readers can intuitively observe the dynamics behavior and better understand the flexibility of the cyclo[18]carbon in the room temperature.

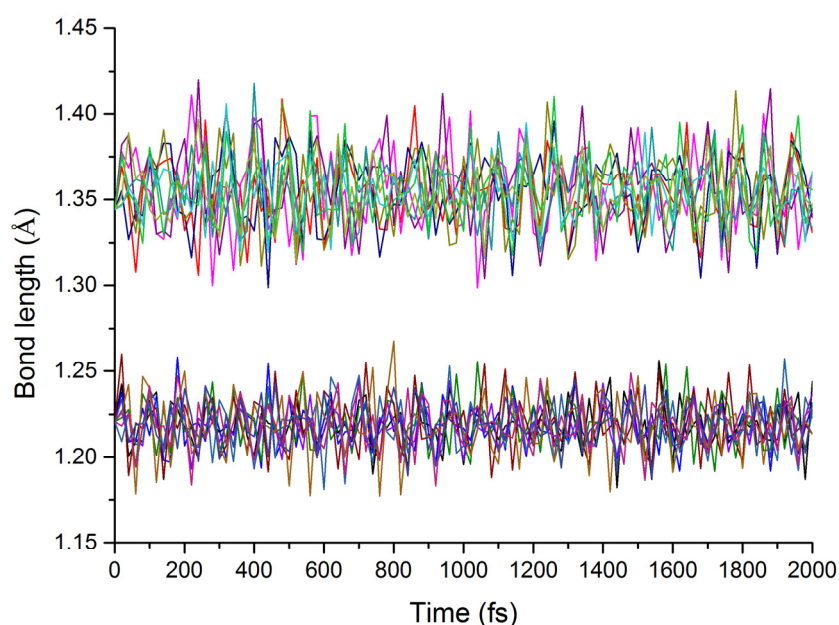


Fig. 26 Variation of all the eighteen C-C bonds of cyclo[18]carbon in the trajectory simulated at 298.15 K. Different bonds are distinguished by different colors. For clarity, the data are plotted every 20 fs.

Next, we examine how the length of the C-C bonds changes during the simulation. Fig. 26 presents variation of all C-C bonds of cyclo[18]carbon in the trajectory simulated at 298.15 K. It can be seen that the bond lengths oscillate notably during the simulation. It is important to note that there is no exchange between different kinds of C-C bonds; in other words, the short C-C bonds are always short C-C bonds, the long C-C bonds are always long C-C bonds. This phenomenon sufficiently demonstrates that the C-C exchange isomerization cannot occur in room temperature, at least in the case that tunneling effect is not taken into account. From Fig. 26 one can also find that fluctuation range of the length of the long C-C bonds is slightly higher than that of the short C-C bonds, indirectly reflecting that the PES along the long C-C bonds is relatively more flat.

Response to electric field: Polarizability and hyperpolarizability

Polarizability and hyperpolarizability are molecular response properties to external electric field. The polarizability measures change of dipole moment before and after applying electric field, while the hyperpolarizability represents nonlinear polarization effect. We computed static polarizability (α), first and second hyperpolarizabilities (β and γ) for the cyclo[18]carbon by coupled-perturbed Kohn-Sham (CPKS) method,^[95] the results are shown in Table 4, the definition of some terms in the table is given below

$$\begin{aligned}\alpha_{\text{iso}} &= (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) / 3 \\ \Delta\alpha &= \sqrt{[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2 + 6(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2)] / 2} \\ \gamma_{\text{tot}} &= \sqrt{\gamma_x^2 + \gamma_y^2 + \gamma_z^2} \\ \gamma_i &= (1/15) \sum_j (\gamma_{ijji} + \gamma_{ijij} + \gamma_{ijjj}) \quad i, j = \{x, y, z\}\end{aligned}$$

where α_{iso} is isotropic polarizability, $\Delta\alpha$ is anisotropy polarizability and γ_{tot} is magnitude of second hyperpolarizability. In order to obtain best estimation for these quantities, the very large LPol-ds basis set was adapted in our calculation in combination with the ω B97XD method. The LPol-ds was specifically developed for high precision evaluation of hyperpolarizability.^[96]

Table 4 Static polarizability and hyperpolarizabilities of cyclo[18]carbon. The molecular orientation is shown in Fig. 1.

Property	Value (a.u.)
α_{iso}	293.9
α_{zz}	97.7
$\alpha_{xx} = \alpha_{yy}$	392.0
$\Delta\alpha$	294.3
β_{tot}	0.0
γ_{tot}	94257.4
γ_{zzzz}	14334.2
$\gamma_{xxxx} = \gamma_{yyyy}$	239152.0

From the $\Delta\alpha$ in Table 4 it can be seen that the cyclo[18]carbon shows strong polarizability anisotropy, the components parallel to the ring (α_{xx} and α_{yy}) are significantly larger than that perpendicular to the ring (α_{zz}), this is expected since cyclo[18]carbon has large number of global delocalized electrons over the ring. The magnitude of first hyperpolarizability (β_{tot}) is exactly zero, this is because this system has central symmetry, it can be demonstrated that all centrally symmetric systems must have vanished hyperpolarizability. However, given that cyclo[18]carbon has strong π delocalization character and thus may be treated as a good π linker, after properly introducing electron donor and acceptor groups onto this system, the resulting cyclo[18]carbon derivatives are hopefully to be employed in nonlinear optics (NLO) material. The data in Table 4 also exhibit that the cyclo[18]carbon has a large second hyperpolarizability, especially in the direction parallel to the ring plane.

Electron ionization, electron affinity and structure reorganization

Table 5 Electron ionization potential (IP), electron affinity energy (EA) and reorganization energy of cyclo[18]carbon

Quantity	Value
Vertical IP	8.34 eV
Adiabatic IP	8.13 eV
Vertical EA	1.79 eV
Adiabatic EA	2.34 eV
Hole reorganization energy	9.8 kcal/mol
Electron reorganization energy	27.0 kcal/mol

In this section, we investigate energy and geometry change during electron ionization and electron affinity processes as well as energy variation caused by structure reorganization in the process of switching electronic states. Relevant quantities are listed in Table 5. In all the calculations, geometry optimizations were finished at ω B97XD/def2-TZVP level, while the single point energy calculations were conducted using a larger basis set aug-cc-pVTZ,^[97,98] which carries abundant diffuse functions and is thus able to well represent anionic state.

As shown in ref. [99], the ω B97XD can nicely reproduce the IP and EA data produced by the much more expensive CCSD(T) level for the systems composed of main group elements. Therefore, our computed vertical and adiabatic ionization potentials (VIP and AIP) as well as vertical and adiabatic electron affinity energies (VEA and AEA) should be reasonable. At the same computational level, the VIP and VEA of benzene are found to be 9.23 eV and -0.69 eV, respectively. A comparison shows that the electrons in the cyclo[18]carbon are less binded than benzene, however, the cyclo[18]carbon has much stronger capacity of capturing an additional electron, as its VEA is positive while VEA of benzene is negative. By the way, the fundamental gap, which is defined as VIP minus VEA, is 6.55 eV for cyclo[18]carbon while 9.92 eV for benzene, implying that the electrons in the cyclo[18]carbon are more easily to be polarized.

The intramolecular hole reorganization energy^[100,101] is a quantification of energy change due to geometry relaxation owing to switching between cationic and neutral states, the electron reorganization energy has similar definition but for switching between anionic and neutral states. It can be seen from Table 5 that electron reorganization energy of the cyclo[18]carbon is significantly larger than the hole reorganization energy, this implies that geometry distorsion caused by electron attachment onto the present system should be much more prominent than that caused by electron detachment.

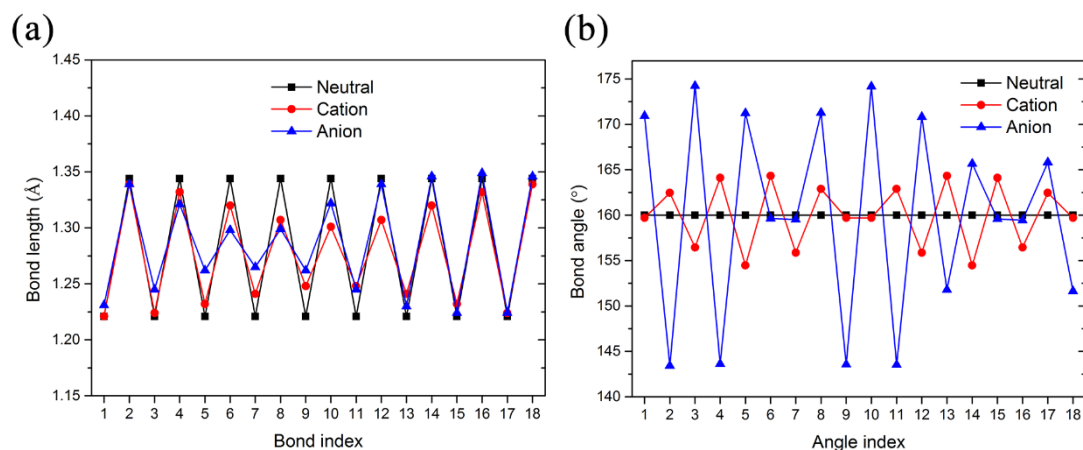


Fig. 27 Bond length and bond angle alternation of cyclo[18]carbon in neutral, cationic and anionic states.

In order to clearly show the geometry difference between the neutral state and charged states of the cyclo[18]carbon, in Fig. 27 we plotted variation curve of bond length and bond angle along its ring for the geometries optimized in neutral, cationic and anionic states. From this figure one can see that the cyclo[18]carbon undergoes obvious geometry distortion after ionization, the extent of distortion is even more heavy if an additional electron is attached to the system; as can be seen clearly from Fig. 27(b), the bond angle fluctuates dramatically in anionic state. The optimized structure of the cationic and anionic states of the cyclo[18]carbon are plotted as Fig. S6, it can be seen that the D_{9h} point group of the neutral state has broken in the charged states.

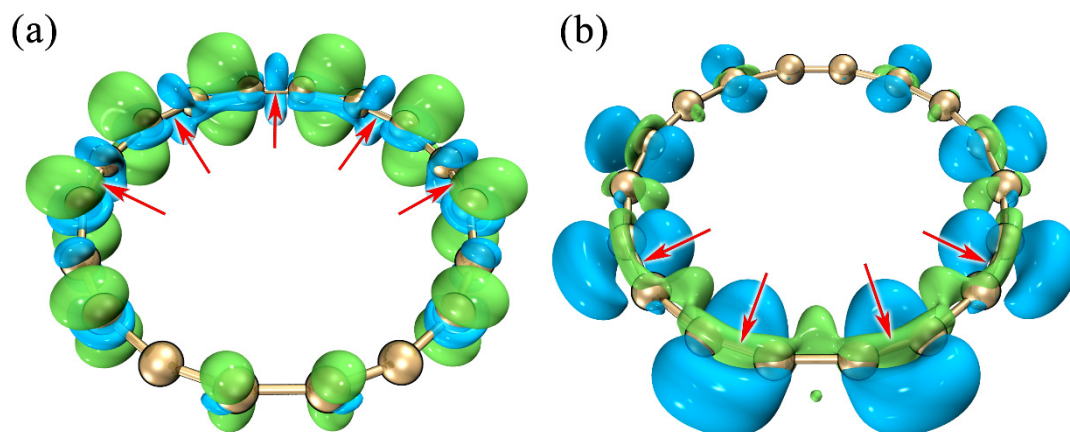


Fig. 28 Isosurface map of electron density at optimized neutral geometry of cyclo[18]carbon (a) $\Delta\rho = \rho_{N+1} - \rho_N$, where N denotes the number of electrons of neutral state (b) $\Delta\rho = \rho_{N-1} - \rho_N$. Green and blue isosurfaces correspond to $\Delta\rho = 0.002$ and -0.002 , respectively. For easy identification, the short C-C bonds are highlighted by arrows.

It is of interest to examine variation of electron distribution during vertical electron ionization and affinity processes for the cyclo[18]carbon, the density difference map is well-suited for this purpose. The isosurface map of $\Delta\rho = \rho_{N+1} - \rho_N$ and $\Delta\rho = \rho_{N-1} - \rho_N$ calculated at ω B97XD/aug-cc-pVTZ level are shown as Figs. 28(a) and 28(b), respectively, where N denotes the number of

electrons in the neutral state. The green regions in Fig. 28(a) clearly indicate that the additional attached electron in the electron affinity process is distributed in the out-plane π region. If comparing this map with the LUMO map in Fig. S7, it can be found that the distribution of the increased electron density is basically identical to the density of LUMO. Hence it can be considered that the extra electron in the anionic state basically occupies the LUMO of the neutral state. The electron affinity process is also accompanied by reorganization of the electron distribution in neutral state because the interaction potential between the electrons is perturbed, therefore in the Fig. 28(a) there are some regions where electron density is decreased. Fig. 28(b) represents how electron distribution varies in the process of vertical ionization, from the blue regions it can be clearly observed that the ionized electron solely comes from in-plane π MOs. If further comparing this figure with Fig. S7, it will be found that the electron ionization from the neutral state to the cationic state can be approximated as electron lost from HOMO orbital.

Other molecular properties

Finally, in Table 6 we present a collection of frequently involved molecular properties for the cyclo[18]carbon.

Table 6 Theoretically evaluated some molecular properties of cyclo[18]carbon

Quantity	Value
Dipole moment	0.000 Debye
Q_{zz}^a	-1.175 Debye·Å
$Q_{xx}=Q_{yy}^b$	0.586 Debye·Å
Mulliken electronegativity	5.07 eV
Chemical potential	-5.07 eV
Fundamental gap (Hardness)	6.55 eV
Softness	0.15 eV ⁻¹
Electrophilicity index	1.96 eV
Nucleophilicity index	2.99 eV
Hydration free energy (298.15 K) ^c	7.3 kcal/mol
LogP (298.15 K)	4.71
Strain energy (298.15 K)	57.7 kcal/mol
NMR chemical shift ^d	127.7 ppm

^a Component of traceless quadrupole moment in the direction perpendicular to the ring

^b Component of traceless quadrupole moment in the direction parallel to the ring

^c From gas phase standard state (1 atm) to solution standard state (1 M)

^d In chloroform environment represented by SMD solvation model

Due to the centrosymmetric character of the cyclo[18]carbon, its dipole moment is exactly zero. The lowest order of multiple moment of this system is quadrupole moment. The traceless quadrupole moment tensor of the cyclo[18]carbon shown in Table 6 was evaluated via ω B97XD/aug-cc-pVTZ. Using the aug-cc-pVTZ instead of the def2-TZVP is because diffuse function is crucial in accurately determining molecular electric multipoles. The data in Table 6 show that the components of traceless quadrupole moment in the directions perpendicular and parallel to

the ring is an evident negative value and a modest positive value, respectively. This phenomenon is similar to benzene, showing that the electron density distribution is elongated in the direction perpendicular to the molecular plane compared to the other orthogonal directions. The reason should be attributed to the fact that the cyclo[18]carbon has globally delocalized out-plane π electrons as benzene.

The Mulliken electronegativity,^[102] chemical potential,^[103] electronic hardness (equivalent to fundamental gap)^[104], electronic softness^[105] and electrophilicity index^[106] were directly obtained by simple algebraic operation based on the vertical IP and EA in Table 5. Theory backgrounds and practical meanings of these quantities can be found in review articles about the conceptual density functional theory.^[107-110] The nucleophilicity index is defined as HOMO level of current system minus that of tetracyanoethylene (TCE),^[111] it reflects ability of a molecule donating electrons. In our calculation the two HOMO levels are obtained at ω B97XD/def2-TZVP level, in contrast to the B3LYP/6-31G* level employed in ref. [111].

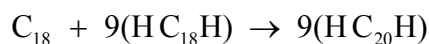
The hydration free energy of the cyclo[18]carbon was calculated based on SMD implicit solvation model,^[112] M05-2X/6-31G* was employed in this calculation since in the original paper of SMD model it was shown that this level is most suitable to be used in conjunction with the SMD model to estimate solvation free energy. The evidently positive value (9.2 kcal/mol) of the hydration free energy should be attributed to the low polarity nature of the cyclo[18]carbon, it suggests that the cyclo[18]carbon is almost completely insoluble in water.

The octanol-water partition coefficient (LogP) of the cyclo[18]carbon was calculated as

$$\log P_{\text{oct/wat}} = -\frac{\Delta G_{\text{solv}}(\text{octanol}) - \Delta G_{\text{solv}}(\text{water})}{2.303RT} = -\frac{E_{\text{octanol}} - E_{\text{water}}}{2.303RT}$$

where ΔG_{solv} is solvation free energy, R is ideal gas constant, the temperature (T) is set to 298.15 K in the present calculation, E_{octanol} and E_{water} are single point energies evaluated under the n-octanol and water environments represented by the SMD model at M05-2X/6-31G* levels, respectively. The calculated LogP is much larger than unity, implying that the cyclo[18]carbon can be easily extracted from water by low polar organic solvents. It is noteworthy that the LogP is well correspond to the MPI index shown earlier, which suggests the cyclo[18]carbon is a very low polar molecule and thus has high affinity with nonpolar substances.

Strain energy of a ring molecule is usually calculated by properly designing a homodesmotic reaction,^[113] it reflects energy difference between the current structure and the fictitious status in which geometry distortion caused by the cyclization is fully released. The strain energy of the cyclo[18]carbon in Table 6 is calculated as negative of reaction enthalpy of below reaction at standard condition:



where HC_{18}H and HC_{20}H are linear polymer molecules containing long C-C chain capped by two hydrogens at their both sides. We employed them in our designed reaction because the chemical environment of the C-C bonds in these systems is similar to that in the cyclo[18]carbon. The calculated strain energy (57.7 kcal/mol) is fairly large, showing that the cyclo[18]carbon have conspicuous intrinsic tendency to open the ring. This observation is fully understandable, because ideal status of the carbons in the cyclo[18]carbon is sp hybridization, which strongly favors linear configuration over bent configuration.

The bond dissociation energy (BDE) is an important property of chemical bonds. However, since the cyclo[18]carbon is a cyclic system and has electronic conjugation feature, it is difficult to divide it into fragments to calculate BDE in usual way. Fortunately, in ref. [44] it was demonstrated that Laplacian bond order (LBO) has very nice linear relationship with BDE for C-C bonds. We performed linear fitting between experimental BDE^[114] and the LBO calculated based on ω B97XD/def2-TZVP level for ethane, ethene and acetylene, see Fig. S8. It can be seen that the linear relationship is perfect, implying that it is fully possible to estimate BDE of the two kinds of C-C bonds via the fitted equation $\text{BDE (kJ/mol)} = 338.08 \times \text{LBO} + 19.70$. By substituting the LBO of the short and long C-C bonds (2.451 and 1.696, respectively, as shown in Table 2) into the formula, it is found that their BDEs are 848.3 and 593.1 kJ/mol, respectively.

The NMR chemical shift of the carbons in the cyclo[18]carbon with respect to tetramethylsilane (TMS) was calculated at ω B97XD/def2-TZVP level in the chloroform environment represented by SMD model. The result 127.1 ppm has the same order of magnitude as the carbon in most organic systems.

4. Summary

Although cyclo[18]carbon was predicted by theoretical chemists since half a century ago, only very recently this system was first experimentally observed and characterized in condensed phase. The unique mono-ring structure and the double 18-center π delocalization character bring many fascinating features to this system. Despite that there have been some theoretical works that studied the cyclo[18]carbon, the present article is the first extremely comprehensive and in-depth theoretical investigation of almost all chemical and physical characteristics of this system. The scope of our study includes

- (1) Geometry characteristics
- (2) Electronic structure, including bonding nature, electron delocalization and aromaticity
- (4) Electrostatic potential
- (5) Dimer structure and π - π stacking interaction
- (6) Reactivity
- (7) Electronic transitions and UV-Vis spectrum
- (8) Vibrational modes as well as IR and Raman spectra
- (9) Molecular dynamics behavior
- (10) Response properties
- (11) Electronic gaining and lossing processes
- (12) Various molecular properties.

This work sheds light on many unknown while intriguing characteristics of the cyclo[18]carbon, we hope that this work could significantly deepen the researchers' understanding of this system, thereby facilitating practical utilization of the cyclo[18]carbon and design of its various useful derivatives.

The Cartesian coordinate of the minimum point of the cyclo[18]carbon in its neutral, cationic and anionic states, as well as its dimer structure have been provided in Section S8 of supplemental material

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