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2019-11-07

V. Baryshnikov , G , Valiev , R , Kuklin , A , Sundholm , D & Ågren , H 2019 , ' Cyclo[18]carbon : Insight into Electronic Structure, Aromaticity and Surface Coupling ' , Journal of Physical Chemistry Letters , vol. 10 , no. 21 , pp. 6701-6705 . <https://doi.org/10.1021/acs.jpcllett.9b02815>

<http://hdl.handle.net/10138/321646>

<https://doi.org/10.1021/acs.jpcllett.9b02815>

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Cyclo[18]Carbon: Insight into Electronic Structure, Aromaticity and Surface Coupling

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ABSTRACT: Cyclo[18]carbon (C₁₈) is studied computationally at density functional theory (DFT) and *ab initio* levels to obtain insight into its electronic structure, aromaticity, and adsorption properties on a NaCl surface. DFT functionals with a small amount of Hartree-Fock exchange fail to determine the experimentally observed polyynic molecular structure revealing a cumulene-type geometry. Exchange-correlation functionals with a large amount of Hartree-Fock exchange as well as *ab initio* CASSCF calculations yield the polyynic structure as the ground state while the cumulene structure as a transition state between the two inverted polyynic structures through a Kekule distortion. The polyynic and the cumulene structures are found to be doubly Hückel aromatic. The calculated adsorption energy of cyclo[18]carbon on the NaCl surface is small (37 meV/C) and almost the same for both structures implying that the surface does not stabilize a particular geometry.

Carbon is one of the most diverse elements of the periodic table with respect to possible allotropes.^{1,2} Among them sp³-hybridized diamond, multilayered sp²-hybridized graphite and monolayer graphene, fullerenes and nanotubes, sp-hybridized **carbyne**, and linear polyynes^{3,4} are most attractive materials and unique objects for practical applications and theoretical surveys.⁵⁻⁷ The number of hypothetically predicted carbon allotropes reaches more than five hundred different structures in accordance with the SACADA database⁸ last updated on May 2017. Nevertheless, carbon allotropes are still in focus of synthetic attempts and theoretical predictions.⁹⁻¹⁵ One of the most impressive recent achievements in this field is the successful synthesis and characterization of the closed-circle polyynic containing 18 sp-hybridized carbon atoms, called cyclo[18]carbon.¹⁶ It is notable that cyclo[18]carbon possesses the special "double" aromaticity¹⁷ because of delocalization of two scaffolds of 18 π -electrons oriented in the plane of C₁₈ ring (18 π_{in}) and perpendicular to it (18 π_{out} , Figure 1) that was first mentioned by Diederich *et al.*¹⁸ and developed further by Fowler *et al.*¹⁹

Numerous electronic structure calculations of cyclo[18]carbon molecule have been carried out at the different levels of theory including the HF,^{18,20} SCF,²¹⁻²³ MCSCF,²⁴ MP2,^{21,22} DFT,^{19,21,25-32} quantum Monte Carlo (QMC)²⁴ and CCSD^{23,29} levels. Surprisingly, only the HF, QMC and CCSD methods yield the polyynic structure that experimentally has been observed in high-resolution atomic

force microscopy (AFM) measurements of cyclo[18]carbon adsorbed on bilayer NaCl on Cu(111) surface at the temperature of 5 K.¹⁶ Most of the common DFT functionals^{19,21,25-32} (B3LYP, BLYP, PBE0, etc.) as well as MP2 calculations²¹ yield the **non-bond-length alternating** cumulene structure of cyclo[18]carbon. Torelli and Mitas explained that DFT fails to produce correct results due to the overestimation of electronic correlation effects at the expense of exchange,²⁴ while Houk and Planner proposed that the incorrect MP2 results are caused by an RHF→UHF instability (*i.e.*, MP2 energies are inaccurate, because the RHF wave function is unstable with respect to the UHF wave function).²⁰ Here, we support the notion of Torelli and Mitas by demonstrating that increasing the Hartree-Fock exchange part in an exchange-correlation functional leads to the experimentally observed polyynic structure of cyclo[18]carbon; *ab initio* CASSCF calculations also exhibit the correct polyynic structure. We utilized the gauge-including magnetically induced currents (GIMIC) approach^{33,34} to investigate the magnetically induced current density and the "double" aromaticity of cyclo[18]carbon beyond the previously published NICS²⁸ and ipsocentric CTOCD-DZ¹⁹ (continuous transformation of origin of current density – diamagnetic zero) studies. The idea that the cumulenic structure of cyclo[18]carbon is the ground-state structure in the gas phase in isolated form, while surface interaction may induce stabilization of the polyynic-type structure has been investigated and disproved by simulations of cyclo[18]carbon adsorption on the NaCl (100) surface within periodic boundary conditions (PBC)

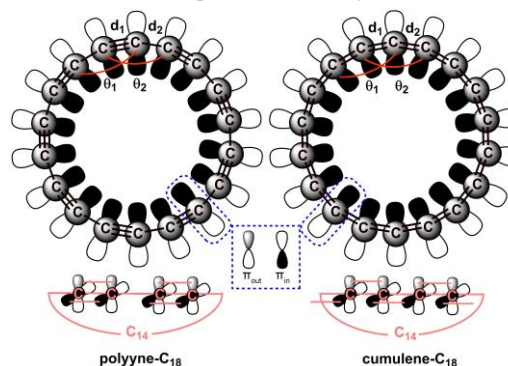


Figure 1. Polyynic and cumulenic structure of cyclo[18]carbon.

Table 1. Selected structural parameters of the ground state polyynic and transition state cumulenic forms of cyclo[18]carbon calculated at the different levels of theory.

	polyynic (C_{9h} , ground state)					cumulenic (C_{9h} , transition state)				
	d_1 , Å	d_2 , Å	θ_1 , °	θ_2 , °	ω_1 , cm^{-1}	d_1 , Å	d_2 , Å	θ_1 , °	θ_2 , °	ω_1 , cm^{-1}
M06-2X	1.226	1.346	160	160	59	1.278	1.277	163	157	1683i
BMK	1.235	1.332	160	160	61	1.279	1.278	163	157	1200i
BHandHLYP	1.223	1.346	159	161	59	1.271	1.271	169	151	1553i
wB97XD	1.223	1.346	159	161	59	1.277	1.277	169	151	1743i
CASSCF(8,8)	1.199	1.356	160	160	59	1.265	1.265	161	159	1900i

The following exchange-correlation functionals (see supporting information (SI) for details) with increased percentage of Hartree-Fock exchange (HFE) relative to the common B3LYP functional (20% HFE) have been selected to probe the ground state structure of cyclo[18]carbon: BMK (42% HF), M06-2X (54% HFE), BHandHLYP (50% HFE) and wB97XD (22% short-range HFE, range separation parameter $\gamma=0.2$). All of them provide the polyynic-type ground state structure of cyclo[18]carbon of the C_{9h} symmetry point group with alternating single and triple C-C bonds (the corresponding structural parameters are collected in Table 1). No significant bond angles alternating θ_1 and θ_2 was observed. The typical deviations are less than 1°. All calculated vibrational frequencies were found to be real (ω_1 is real and positive in Table 1) for all cases of polyynic cyclo[18]carbon indicating the true energy minimum whereas one imaginary frequency was obtained for the cumulenic structure.

In favor of the hypothesis that increased contribution of HFE affects the ground-state geometry of large cyclo[4N+2]carbon molecules ($N=4-8$), we refer to the study by Remya and Suresh²⁸. They used the meta-GGA M06L local functional with zero 0% HFE, which revealed a cumulenic ground-state structure for the studied cyclo[4N+2]carbons ($N=4-8$) including cyclo[18]carbon. In order to estimate the threshold HFE value sufficient to obtain the correct bond alternation in cyclo[18]carbon in the hybrid functional, we performed structural relaxations using two DFT levels (B3LYP/6-311++G(d,p) and HSE06 with plane wave (PW) basis set as described in details in SI) varying the HFE part from 0 to 100%. We found that 37% HFE contribution at the B3LYP/6-311++G(d,p) and 32% HFE within HSE06/PW levels are enough to reproduce the experimentally observed polyynic bond-length alternation of cyclo[18]carbon. Other hybrid functionals used in this work reproduce the HFE trend obtained with the B3LYP and HSE06 reference functionals (Figure S1).

The attempts to optimize the cumulenic-type geometry of cyclo[18]carbon within BMK, M06-2X, BHandHLYP, wB97XD functionals and CASSCF(8,8) calculations with different symmetry constraints always yielded a saddle point with the one or few imaginary frequencies. The calculations suggest that the cumulenic-type geometry might be a transition state structure for a bond shift between two polyynic forms of cyclo[18]carbon with inverted ordering of the single and triple bonds (both of C_{9h} symmetry, Figure 2). Indeed, QST3 optimization of the transition state structure for such a bond shift resulted in a bond-angle alternating cumulenic-type geometry (Table 1) of the same C_{9h} symmetry with one imaginary frequency corresponding to the Kekule-type in-plane C-C stretching vibrations (Figure 2). The calculated energy barrier for the inversion process depends on the method. The BMK functional underestimates the bond shift barrier in comparison to the other levels of theory, demonstrating a barrier of only +3.5 kcal mol⁻¹, while the rest of the functionals (M06-2X, BHandHLYP, wB97XD) as well as CASSCF(8,8) calculations, yield very similar barrier heights of 8.8-12.1 kcal mol⁻¹ (Figure 2). The CASSCF calculations show that the predominant weight of a closed-shell singlet determinant for the polyynic and cumulenic structures is 0.95, implying that single-reference approaches should be applicable.

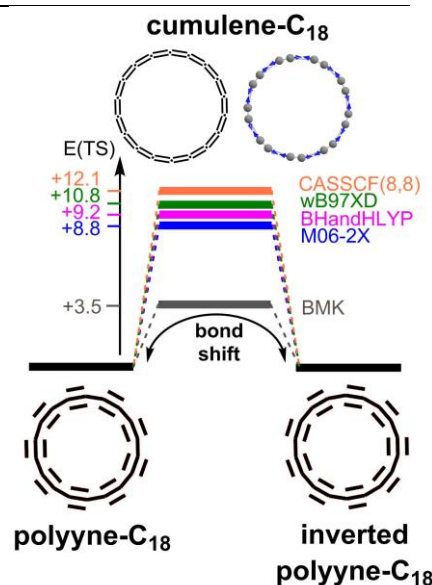


Figure 2. Bond shift mechanism in polyynic cyclo[18]carbon through the cumulenic transition state mediated by Kekule vibrations. The barriers are given in kcal mol⁻¹.

Using the M062X/6-311++G(d,p) optimized ground-state polyynic structure and the transition-state cumulenic geometry, we performed calculations of the magnetically induced ring current strength using the GIMIC approach (see details in the SI). We found that applying an external magnetic field perpendicular to the molecular plane of cyclo[18]carbon induces a strong diatropic ring current of 29 nA T⁻¹ showing that polyynic cyclo[18]carbon is aromatic in agreement with NICS and ipsocentric CT OCD-DZ calculations^{19,28} and the Hückel (4N+2) rule³⁵. For comparison, benzene sustains a net diatropic ring current about 12 nA T⁻¹.³⁴ The signed modulus of the magnetically induced current density (Figure 3) shows that diatropic ring current in polyynic-type cyclo[18]carbon originates from the two scaffolds of 18 π -electrons oriented in- and out- of molecular plane proving the double aromaticity idea.^{18,19} Calculating the ring current strength within reduced contours that cover particular in- and out-of-plane delocalization areas (see details in SI) shows the efficient delocalization of the 18 π_{out} electrons ($I_{out} = 21.8$ nA T⁻¹) and less efficient delocalization of 18 π_{in} electrons ($I_{in} = 7.2$ nA T⁻¹) due to the perpendicular alignment of these orbitals.¹⁹ The cumulenic-type TS structure sustains much higher net diatropic current (73.2 nA T⁻¹) due to the more efficient overlap and delocalization of the π_{in} and π_{out} orbitals. The strengths of the I_{in} and I_{out} currents for the cumulenic structure were also found to be not the same (32.2 and 41 nA T⁻¹, respectively) meaning that the π_{in} and π_{out} orbitals are also not identical with respect to the orbital delocalization. The reason for that is the same as for polyynic-type cyclo[18]carbon: the angular overlapping of 18 π_{in} electrons results in less efficient delocalization comparing to the perpendicularly oriented 18 π_{out} electrons. Despite the higher aromaticity of transition state cumulenic-

type cyclo[18]carbon its total energy is considerably higher relative to the ground state polyynic-type cyclo[18]carbon. The reason for that argued in terms of the second-order Jahn-Teller effect^{29,32} that overcomes the aromatic stabilization of cumulenic form and hence results in bond-length alternated polyynic structure.

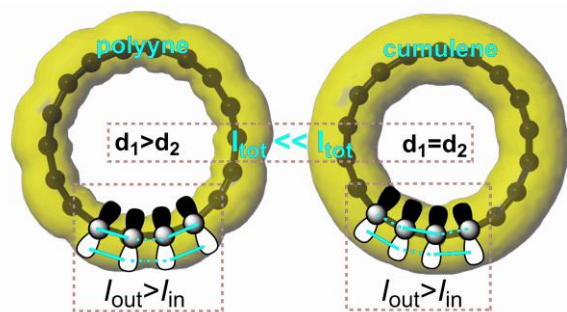


Figure 3. The signed modulus of the magnetically induced current densities for the polyynic and cumulenic cyclo[18]carbon.

In order to elucidate the hypothesis that the cumulenic type geometry is a gas phase global minimum structure, while the polyynic geometry can only exist on the NaCl surface due to extra stabilization effects (relative to cumulenic one), we performed calculations of the adsorption of polyynic- and cumulenic-type cyclo[18]carbon on a NaCl (100) surface using the PBC approximation (see SI for details). The initial 4×4 thin-film models of $\text{Na}_5\text{Cl}_{14}$ superstructure consisting of three atomic layers were obtained from a well-converged NaCl unit cell and then relaxed. We found that the unit cell is large enough to simulate cyclo[18]carbon adsorption on the NaCl surface avoiding spurious interactions between the molecules with an effective separation distance of 9.58 Å between nearest neighboring cyclo[18]carbon molecules. The simulated superstructure is shown in Figure 4a. Regardless of the assumed initial cyclo[18]carbon geometry (cumulenic or polyynic), the final optimized geometry was found to be of cumulenic type when the PBE functional with 0% of HFE was utilized. This confirms once again that functionals like PBE without enough contribution of HFE cannot properly describe geometry and electronic structure of cyclo[18]carbon.³¹

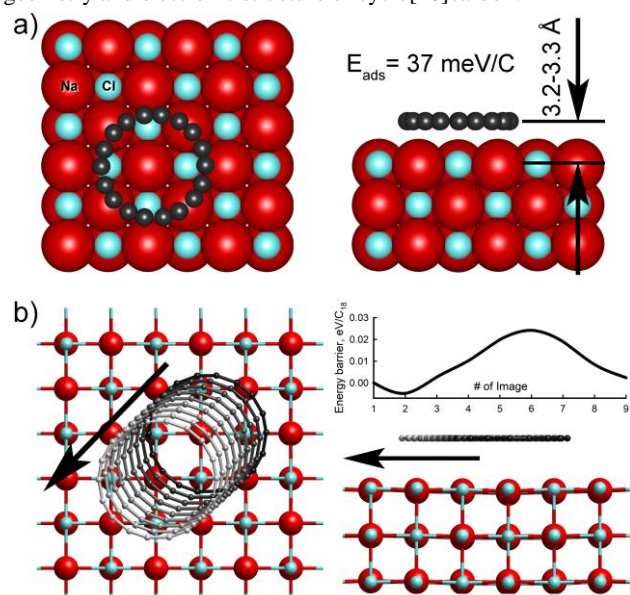


Figure 4. (a) Top (left) and side (right) views of the NaCl supercell with adsorbed cyclo[18]carbon. (b) Results of the NEB simulation of the cyclo[18]carbon mobility along the NaCl surface. The arrows depict the direction of cyclo[18]carbon molecule movement during NEB cycle.

To estimate the adsorption parameters of polyynic cyclo[18]carbon, we used its equilibrium structure obtained at the CASSCF(8,8) level and then fixed all carbon positions but allowed to completely relax the NaCl (100) substrate. Similarly we calculated the cumulenic type but allowing to relax all atoms. We found, that the formation of the $\text{C}_{18}/\text{NaCl}$ heterostructure does not play any significant role in the stabilization of the polyynic structure. The adsorption energies were found to be almost equivalent (37 meV/C) for both cumulenic and polyynic structures. It confirms that there is no surface-induced transition between polyynic and cumulenic structures, because the adsorption energies of both structures are the same. Accounting for the very weak interaction between cyclo[18]carbon and NaCl it is evident that the molecules can freely move along the NaCl surface even at very low temperatures, which is in agreement with experimental observations.¹⁶ Indeed, calculations using the nudge elastic band (NEB) method³⁶ yield a very small energy barrier of 30 meV for the cyclo[18]carbon mobility on the NaCl surface (Figure 4b).

In conclusion, the recently synthesized cyclo[18]carbon molecule has been studied computationally at the DFT and CASSCF levels of theory in order to confirm that the polyynic structure is the global minimum. The cumulenic-type structure of cyclo[18]carbon is found to be a transition state for the single-triple bond inversion process. This interconversion is mediated by the Kekule-type stretching vibration with the estimated energy barrier of around 10 kcal mol⁻¹. An extended amount of Hartree-Fock exchange in the employed functional is crucial for obtaining the experimentally observed polyynic structure of cyclo[18]carbon. The double aromaticity of both polyynic and cumulenic cyclo[18]carbon has been investigated by gauge-including magnetically induced currents calculations, which predict that the **bond-length alternating polyynic** structure is less aromatic than non-alternating transition-state structure due to a less efficient overlap of π_m and π_{ou} orbitals of the polyynic structure. Two molecular structures of cyclo[18]carbon have identical adsorption energies on the NaCl surface, suggesting that there is no extra stabilization favoring polyynic structure as compared to the cumulenic one. NEB simulations show that cyclo[18]carbon can move almost without any barrier on the NaCl (100) surface, which is in agreement with experimental data.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.XXXXXXX. Computational details and corresponding references on the employed methods, bond length dependence on the percentage of HFE contribution within the HSE06 and B3LYP hybrid functionals (PDF).

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Notes

The authors declare no competing financial interests.

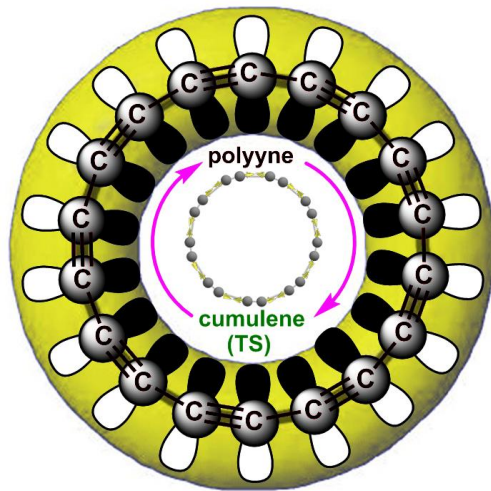
ACKNOWLEDGMENT

This work was supported by the Olle Engkvist Byggmästare foundation (contract no. 189-0223) and by the Ministry of Education and Science of Ukraine (project no. 0117U003908). The calculations were performed with computational resources provided by the High-Performance Computing Center North (HPC2N) in

Umeå, Sweden, through the project “Multiphysics Modeling of Molecular Materials” SNIC 2018-2-38. The GIMIC calculations were carried out using SKIF supercomputer at the Tomsk State University. A.V.K. acknowledges the support of the Russian Science Foundation (Project No. 19-73-10015). R.R.V. thanks the Academy of Finland (1325369) and is also thankful to the Tomsk Polytechnic University Competitiveness Enhancement Program (VIU-RSCABS-142/2019).

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