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Magnetic Properties of Cyclo[*n*]Carbons (*n* = 10–34)

Quantum-chemical calculations of the magnetic properties (magnetically induced ring-current strength, magnetizability) of even- and odd-number cyclo[*n*]carbons (*n* = 10–34) were carried out. The total energy of the studied molecules as a function of the external magnetic field was found for the first time. The obtained dependences predict correctly the magnetic nature of cyclo[*n*]carbons. For even-number aromatic cyclo[*n*]carbons the energy of the system increases with increasing magnetic field, while for antiaromatic systems, the energy decreases. Such behavior indicates that aromatic even-number cyclo[*n*]carbons (*n* = 4*k*+2) are diamagnetic, whereas antiaromatic even-number cyclo[*n*]carbons (*n* = 4*k*) are paramagnetic. These results are confirmed by the previously calculated average magnetizability values. In the case of odd-number cyclo[n]carbons, all structures except C13 are diamagnetic. Antiaromatic C13 is paramagnetic according to average magnetizability calculations. It was shown that nonaromatic cyclo[*n*]carbons (*n* = 28–34) at high magnetic fields (*B* > 300 T) possess a nonlinear effect of the increase in the energy of the system with increasing magnetic field. This effect can be observed experimentally in NMR spectra at a magnetic field greater than 300 T. The performed calculations demonstrate that the HF method correctly predicts the magnetic and aromatic properties of cyclo[*n*]carbons (*n* = 10–34).

Keywords: cyclo[*n*]carbons, magnetizability, magnetically induced current, magnetic properties, aromaticity, chemical calculations, magnetic field.

Introduction

Carbon is a unique chemical element that has the largest number of allotropic modifications, each of them has different chemical structure. As a result, these structures have special physicochemical properties. Cyclo[*n*]carbons are allotropes of carbon formed by sp-hybridized carbon atoms linked in a ring [1]. Cyclo[*n*]carbons can arise as a result of condensation processes in the atmospheres of carbon-rich stars [2]. In addition, they appear as intermediates in the plasma used to produce thin diamond films [3].

The cyclo[18]carbon was firstly observed in 1989, however due to its high reactivity it was difficult to separate and characterize the structure of this compound [4]. Subsequent theoretical studies showed the existence of two different forms of molecules: density functional theory and Møller–Plesset perturbation theory (MP2) calculations indicated alternating cumulene structure with non-bond-length [5, 6], while calculations using the Hartree-Fock method [4], the high-level Monte Carlo, *ab initio* (CASSCF) and coupled clusters methods predicted a structure with alternating conjugated single and triple bonds [7, 8]. In 2019, for the first time, the alternating single and triple bonds structure of cyclo[18]carbon was determined experimentally [9].

Subsequently, density functional calculations revealed that the amount of Hartree-Fock exchange in functional is important to determine the correct structure of cyclo[n]carbons [10]. Thus, functionals with a small amount of Hartree-Fock exchange due to overestimation of the correlation energy predict a cumulene structure, while functionals with a large amount of Hartree-Fock exchange [>40 %], such as M062X, BHHLYP, CAM-B3LYP give the correct structure with alternating conjugated single and triple bonds (polyyne-type structure) [10–12]. In addition, it was shown that the cumulene structure of cyclo[18]carbon is a transition state for the single-triple bond inversion process [10].

Synthesis of cyclo[18]carbon gave rise to intense interest in studying the properties and structure of molecules with a different number of carbon atoms in the ring, including odd-number cyclo[*n*]carbons [13–16]. It was shown that odd-number cyclo[*n*]carbons have a carbene structure with a singlet ground state [16]. It should be noted that cyclo[10]carbon and cyclo[16]carbon have already been synthesized. Successes in the synthesis of these systems point to subsequent syntheses of other forms of cyclo[n]carbons in the future.

The presence of triple bonds in the structure of cyclo[*n*]carbons leads to their high chemical activity. However, despite the high reactivity, studies of spectroscopic, aromatic, structural, mechanical and electronic

properties reveal that cyclo[*n*]carbons are promising materials that can find application in various fields [10, 16–23]. Thus, due to pronounced electron delocalization, cyclo[*n*]carbons exhibit high electron mobility, which makes it possible to consider them as semiconductor materials [19, 20]. Cyclo[*n*]carbon rings can mechanically interlock to form catenanes, which in turn can bind with bioactive molecules and used to deliver drugs [21]. In addition, cyclo[*n*]carbon rings are highly elastic, and their energy gap can vary depending on the deformation of the ring, which can be used in nanomechanical systems and molecular electronic devices [22, 23].

Cyclo[*n*]carbons also have special magnetic properties, which occur due to the double aromaticity of the molecules [10, 24, 25]. Because of the specific structure, molecules have two independent orthogonal conjugated systems located above and in the plane of a molecule. In an external magnetic field cyclo[*n*]carbons sustain magnetically induced ring currents, which determine their magnetic nature. Antiaromatic cyclo[*n*]carbons with *n* = 8, 12, 16, 20, 24 are paramagnetic [26, 27]. As shown in [27], paramagnetism in closed-shell molecules arises due to strong paratropic ring currents ($|I| > 20$ *n*A/T).

The study of ionization potentials, electron affinities, energy gaps between electronic states for cyclo[*n*]carbons (*n* = 8–100) showed that for *n* > 32 the difference in the properties disappears [28]. This can be explained by the fact that for *n* > 32 the electrons are localized on triple bonds. In this case, the distortion of electron delocalization leads to the loss of aromatic properties. Starting from *n* = 34, systems become non-aromatic [26].

Studies of the magnetic properties of cyclo[*n*]carbons mentioned above were carried out within the framework of the quadratic response theory. However, the detailed study of the magnetic field effect on the properties of cyclo[*n*]carbons has not yet been carried out. Today, the progress in quantum-chemical calculations has led to the inclusion of the magnetic field in the software. Recently, the codes have been implemented in BAGEL and TURBOMOLE [29]. It should be noted that BAGEL implements Dirac equation calculations which allows taking into account relativistic effects [29].

The aim of this work was to study the magnetic properties of a series of the odd- and even-number cyclo[*n*]carbons (*n* = 10–34) in an external magnetic field using quantum chemistry methods.

Computational Details

Previously, it was mentioned that the Hartree-Fock (HF) method correctly predict the polyyne structure of cyclo[*n*]carbons. In addition, the amount of Hartree-Fock exchange in the density functionals plays a decisive role in predicting the structural and magnetic properties of cyclo[*n*]carbons [10]. Therefore, we used the Hartree-Fock (HF) method to study the properties of cyclo[*n*]carbons in an external magnetic field. The optimized structures of the studied cyclo[*n*]carbons (*n* = 10–34) were taken from [16, 26]. Structures with an even-number of carbon atoms were optimized at the DFT level using the M06-2X functional and the def2-TZVP basis set [26]. Cyclo[*n*]carbons with an odd-number of carbon atoms were optimized at the *ab initio* complete active space self-consistent field (CASSCF) level with the 6-31G(d, p) basis set [16]. All of the studied cyclo[*n*]carbons have a polyyne structure. The energy of systems in an external magnetic field was calculated at the HF level of theory using split-valence polarization basis sets (SVP) [30] with the BAGEL program [31].

Magnetically induced ring currents were calculated using the GIMIC method, which uses as input data the atomic orbital density matrix, the perturbed atomic orbital density matrices and the basis-set information [32, 33]. The density matrices were obtained by performing nuclear magnetic resonance (NMR) shielding calculations. The density matrices were computed at the HF/def2-TZVP [34] level using Gaussian 09 [35]. The strengths of the ring currents (*n*A/T) were computed by integrating the current-density flux that passes through a plane placed perpendicular to the molecular plane. We evaluated the accuracy of HF ring current calculations by comparing the results with previously calculated magnetically induced currents obtained at the M06-2X level [27]. The choice of the M06-2X [36] functional is due to its ability to correctly calculate the strength of ring currents, including strongly antiaromatic species [10].

The obtained curves of the dependence of the molecular energy on the magnitude of the external magnetic field were used to calculate the magnetic susceptibility:

$$\chi = -\frac{\partial^2 E}{\partial B^2},$$

where *E* — the total energy; *B* — the magnetic field.

The magnetic susceptibility results were compared with the Gaussian magnetic susceptibility results obtained for even-number cyclo[*n*]carbons at the M06-2X/def2-TZVP level [36]. The magnetic susceptibility

for odd-number cyclo[*n*]carbons was obtained for the first time at the M06-2X/def2-TZVP level. Calculations were carried out using Gaussian 09 [35].

Results and Discussion

We investigated molecular properties for even- and odd-number cyclo[*n*]carbons from C_{10} to C_{32} and C_{34}. Molecular structures of the studied cyclo[n]carbons are presented in Figure 1.

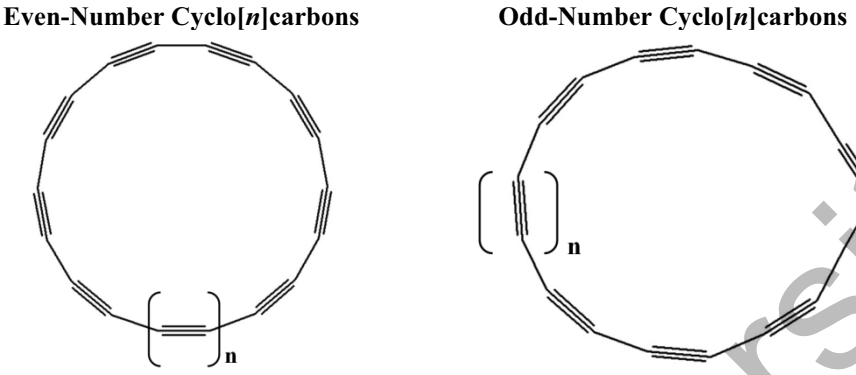


Figure 1. Molecular structures of the studied cyclo[n]carbons

As can be seen in Figure 1, the odd-number cyclo[*n*]carbons have an extra carbon atom, which leads to a specific geometry with a sharp angle at the carbene atom of these systems. Despite this fact, all odd-number cyclo[*n*]carbons are planar.

The results of magnetically induced current and magnetizability calculations for the studied cyclo[*n*]carbons are presented in Tables 1−2. The dependence of the molecular energy on the magnetic field is shown in Figure 2.

Table 1

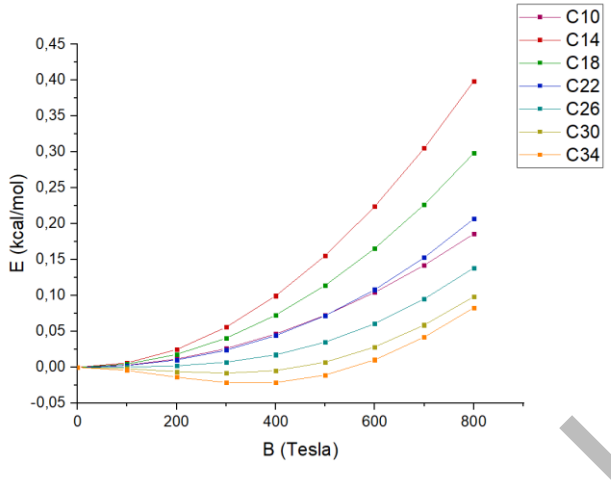
Magnetically induced ring-current strength of the studied cyclo[n]carbons

Even-number	*I*, *n*A/T		Odd-number	*I*, *n*A/T	
C_n	HF	M062X	C_n	HF	M062X
10	24.5	29.2	11	10.8	12.3
12	–18.6	–40	13	–8.3	–27
14	30.5	43.2	15	5.8	9
16	–13.1	–36.1	17	–3.5	–12.8
18	13.8	31.6	19	2.5	5.5
20	–7.1	–27.1	21	–1.3	–5.7
22	6.4	18.1	23	1.03	1.7
24	–3.6	–18.4	25	–0.5	–1.8
26	3	10.5	27	0.4	0.8
28	–1.7	–15.3	29	–0.1	–0.7
30	1.5	6.4	31	0.3	0.5
32	–0.8	–4.3			
34	0.7	5.0			

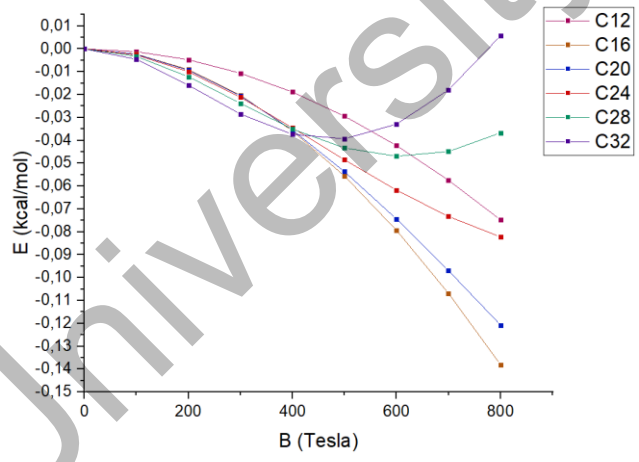
As can be seen in Table 1, that even-number cyclo[*n*]carbons satisfy Hückel's rule. Cyclo[*n*]carbons ($n = 4k+2$) sustain the net diatropic currents, indicating their aromatic character, while cyclo[*n*]carbons ($n = 4k$) are clearly antiaromatic, sustaining a net paratropic ring currents. Odd-number cyclo[*n*]carbons satisfy the following aromaticity rule: the systems with $n = 4k+1$ are antiaromatic, whereas ones with $n = 4k+3$ are aromatic. In the series of even-number cyclo[n]carbons, the most aromatic is C_{14} with diatropic ring currents of 43.2/30.5 nA/T at the M062X/HF levels. The most antiaromatic is C_{12} with a total paratropic ring current of –40.0/–18.6 nA/T at the M062X/HF levels. In the case of odd-number cyclo[n]carbons, the most aromatic is C_{11} with a ring current of 12.3/10.8 nA/T at the M062X/HF levels, while

the most antiaromatic is C_{13} with a ring current of –27.0/–8.3 *n*A/T at the M062X/HF levels. As n increases, the ring-current strength in cyclo[*n*]carbons decreases. In contrast to even-number cyclo[*n*]carbons, odd-number cyclo[*n*]carbons are generally less aromatic/antiaromatic that is confirmed by weaker ring currents. Starting from $n > 21$ odd-number cyclo[*n*]carbons become nonaromatic ($|I|<3$ *n*A/T).

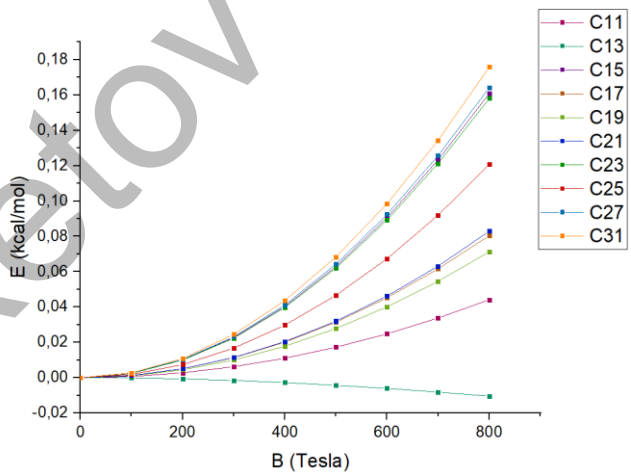
The results obtained at the HF level correctly assess the aromatic character of cyclo[*n*]carbons. The ring-current strength for cyclo[*n*]carbons with $n = 10$, 11 obtained at the HF level agree with the results of M062X calculations. However, there is a strong discrepancy in ring-current strengths for the HF and M062X calculations as n increases. The HF predicted ring-current strengths are generally much smaller than ones obtained at the M062X level. The largest cyclo[*n*]carbon possessing aromatic properties according to HF calculations is the antiaromatic C_{24}, which has the net paratropic ring current of –3.6 *n*A/T, whereas the M062X provides for C_{24} the ring current of –18.4 *n*A/T. In the case of odd-number cyclo[*n*]carbons, C_{17} has the ring current of –3.5 *n*A/T (–12.8 *n*A/T at the M062X level). The subsequent odd-number cyclo[*n*]carbons ($n > 17$) and even-number cyclo[*n*]carbons ($n > 24$) are already nonaromatic.



a) aromatic even-number cyclo[*n*]carbons;



b) antiaromatic even-number cyclo[*n*]carbons;



c) odd-number cyclo[*n*]carbons

Figure 2. The energy dependence of cyclo[*n*]carbons (C_n) on the magnetic field

Figure 2 demonstrates the change in the energy of the system depending on the magnetic field. It is clearly seen that the change in energy for aromatic and antiaromatic even-number cyclo[*n*]carbons is different. For aromatic cyclo[*n*]carbons ($n = 4k + 2$), the energy of the system increases with increasing magnetic field. This dependence indicates a diamagnetic character of aromatic cyclo[n]carbons, which is confirmed by the average magnetizability calculations (Table 2). Another picture is observed for antiaromatic even-number cyclo[*n*]carbons. The energy of antiaromatic species ($n = 4k$) decreases with increasing the magnetic field.

Such a decrease in energy indicates the paramagnetic nature of antiaromatic cyclo[*n*]carbons, which is also confirmed by calculations of average magnetizabilities (Table 2).

Table 2

Average magnetizability of the studied cyclo[*n*]carbons

Even-number C_n	χ, a.u.		Odd-number C_n	χ, a.u.	
	HF	M062X		HF	M062X
10	–51	–25	11	–12	–19
12	22	14	13	3	3137
14	–54	–57	15	–44	–13
16	40	18	17	–23	–113
18	–78	–68	19	–20	–63
20	41	16	21	–23	–60
22	–44	–63	23	–43	–56
24	46	7	25	–32	–56
26	–6	–70	27	–45	–54
28	58	–6	29	–41	–41
30	36	–66	31	–47	–46
32	82	–20			
34	79	–61			

An interesting trend is the energy changes occurs when C_{28}-C_{34} cyclo[*n*]carbons lose their aromatic/antiaromatic properties and become nonaromatic at high magnetic field. At magnetic fields B > 300 T for C_{30}, C_{34} and B > 400 T for C_{32} and B > 600 T for C_{28}, the energy of the systems begins to increase. This indicates that nonaromatic systems at high magnetic fields change their magnetic nature from paramagnetic to diamagnetic. Such changes in energy indicate the effects that can arise in NMR spectra at high magnetic field.

Regarding the odd-number cyclo[*n*]carbons, the energy of these systems increases with increasing magnetic field. The exception is the antiaromatic C_{13}, for which the energy decreases with increasing magnetic field. Thus, we can conclude that all odd-number cyclo[*n*]carbons are diamagnetic with the exception of C_{13}, which exhibits a paramagnetic nature. These observations are confirmed by calculations of the average magnetizabilities (Table 2). The surprisingly large value of the average magnetizability 3137 a.u. (at the M062X level) is observed for C_{13}. The paramagnetic nature of C_{13} arises from the large value of the paratropic ring current (–27 nA/T at the M062X level).

According to the results presented in Table 2, the magnetizability values obtained from the dependence of energy on the magnetic field are in good agreement with the results obtained at the M062X level. Differences in the results are observed for nonaromatic cyclo[*n*]carbons C_{28}-C_{34}, in which there is a deviation in the energy change at high magnetic field. The results of magnetizability calculations based on the dependence of energy on the magnetic field determine these structures as paramagnetic, while the results at the M062X level indicate their diamagnetic nature. The reason may be the fact that the calculation of magnetizability was carried out in the range of 0 to 50 T, where the energy of the systems decreases with increasing magnetic field. In general, the obtained dependences of the energy of the system on the magnetic field correctly predict the magnetic properties of cyclo[*n*]carbons.

Conclusions

In this work, the magnetically induced ring-current strengths and magnetizabilities for a series of cyclo[*n*]carbons (*n* = 10–34) were computed. The calculations reveal that the dependence of the total energy of studied even-number cyclo[*n*]carbons on the magnetic field is determined by their aromatic character. For aromatic molecules the energy increases with growth of magnetic field, while for antiaromatic molecules the energy decreases. An unusual effect is observed for nonaromatic C_{28}-C_{34} cyclo[*n*]carbons. The feature is that the energy for these system decreases in the range of 0 to 300-600 T and increase for higher magnetic fields. Another case occurs for odd-number cyclo[n]carbons. For these molecules the total energy increases with growth of magnetic field regardless of their aromatic character. The exception is the strongest antiaromatic C_{13}.

It is important to note, that the results of calculations obtained by the HF method are generally consistent with more accurate M062X level of theory. Therefore, the HF method correctly predicts the magnetic and aromatic properties of cyclo[n]carbons.

It should be noted that BAGEL implements multiconfiguration calculations at the CASSCF (Complete Active Space SCF) level of theory. In the future, CASSCF method can be applied to provide high-level theory calculations of the structural and magnetic properties of cyclo[*n*]carbons in an external magnetic field.

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