

Prediction of a Cyclic Helical Oligoacetylene Showing Anapolar Ring Currents in the Magnetic Field

Raphael J. F. Berger

Paris-Lodron Universität Salzburg, Fachbereich für Materialwissenschaften und Physik,
Hellbrunnerstr. 34, A-5020 Salzburg, Austria

Reprint requests to Dr. Raphael J. F. Berger. Fax: +43-662-8044-622.

E-mail: raphael.berger@sbg.ac.at

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The first representative of a possible new class of conjugated cyclic polyacetylenes is predicted using DFT calculations. These species have a helical secondary structure and a closed-shell electronic ground-state configuration. Molecular and spectroscopic properties are discussed, and a distinct anapolar ring current structure in a constant and homogeneous magnetic field, perpendicular to the main molecular plane is demonstrated.

Key words: Anapole, [144]-Annulene, Computational Chemistry, Molecular Ring Current, Hydrocarbon

Introduction

Studying magnetically induced molecular ring currents can aid in understanding the chemical nature of molecules with non-classical bonding [1–3]. In many cases the topology of the molecular ring currents provides elegant interpretations for NMR spectra [1, 3]. With an increase in the use of standardized quantum-chemical programs that enable chemists to calculate magnetically induced molecular ring currents [4], new and interesting results are to be expected. A recent example is the direct correlation between bond-strength and vortex-current strength in hydrogen bonds [5, 6]. Although good physical and mathematical descriptions governing molecular ring currents have been known for some time [7–10], many questions, especially concerning their connection to chemical properties, remain open. The present work does not focus specifically on these questions, but it shows how a consideration of molecular ring currents can contribute to the discovery of hitherto unknown compounds having unusual magnetic properties. Pelloni and coworkers reported on the “quest of molecular anapoles” [11]. We demonstrate how a molecule with an anapolar ring current structure can be designed and predict molecular and spectroscopic properties of

this molecule based on results from quantum-chemical calculations.

Results and Discussion

When a molecule *M* is placed in an external magnetic field, **B**, which is in the simplest case a constant, weak and homogeneous field, an inductive response results. This is, in the first instance, the induced electronic current probability density **j**. In turn, **j** induces a magnetic field **B**_{ind}. When **B**_{ind} enhances **B** inside *M* (enhancing the density of the magnetic field lines inside *M*), *M* is called paramagnetic. When **B** is diminished inside *M* by **B**_{ind} (diminishing the density of the magnetic field lines inside *M*), *M* is termed diamagnetic. A third theoretical possibility is that **B** is neither enhanced nor diminished by **B**_{ind}, but that only a local rotation of the magnetic field lines is induced. Fig. 1(a) shows schematically a diamagnetic ring current topology in an external magnetic field. It is typical for aromatic ring systems like benzene. **B**_{ind} is, here, opposed to **B**, and a magnetic dipole moment is induced. Such ring currents are called diatropic or simply “dipolar ring currents”. In Fig. 1(b) anapolar ring currents, inducing a different ring-shaped magnetic field, **B**_{ind} a so called “magnetic anapole moment” [11–15],

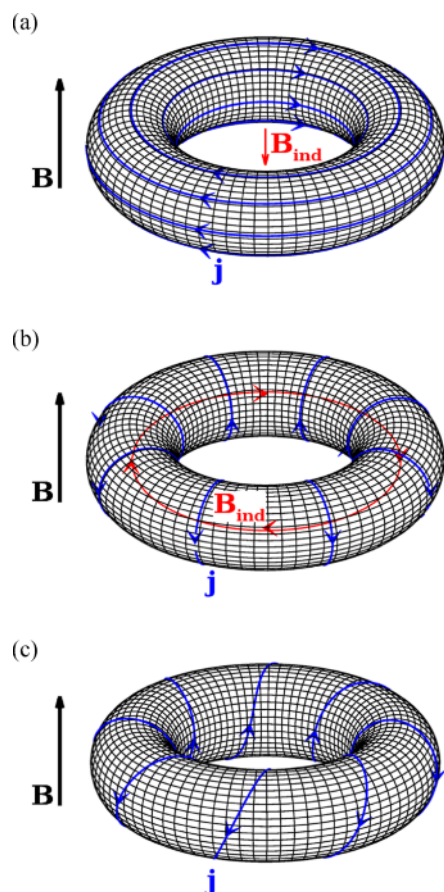


Fig. 1 (color online). (a) Diamagnetic ring current structure induced by an external magnetic field \mathbf{B} . The back-induced magnetic field \mathbf{B}_{ind} (red vector) inside the ring current is opposed to \mathbf{B} . A magnetic dipole moment is induced, hence such currents are called dipolar or diatropic; (b) anapolar ring currents \mathbf{j} (blue), inducing a magnetic anapole moment parallel to \mathbf{B} ; (c) superposition of dipolar and anapolar currents.

are shown. A superposition of dipolar and anapolar currents results in a ring current pattern as shown in Fig. 1(c).

For the dedicated design of a molecular species showing an anapolar ring current pattern in a magnetic field, one can make use of the observation that closed-loop currents appear around functionalities with delocalized electron bonding. The simplest case might be a covalent bond with a vortex between the bonded atoms or a monocyclic aromatic molecule. This holds true to a certain extent even when the magnetic field and the plane of delocalization are not orthogonal. For instance, when a benzene molecule is oriented at a 45°

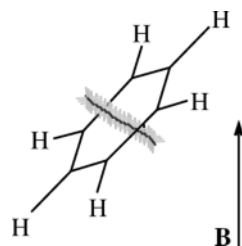


Fig. 2. The molecular plane and the external magnetic field (\mathbf{B}) are forming an angle of 45° . In the center of the benzene molecule some points are shown where the induced current strengths is approaching 0. These so called “stagnation points” are highlighting the region of the innermost current vortex. It can be seen that this vortex is not parallel to \mathbf{B} but that it forms a comparably large angle of approximately 75° with the molecular plane.

angle (instead of the commonly used 90° angle) with respect to the magnetic field as it is shown in Fig. 2, the innermost current vortex in the center region of the molecule still has a relatively large angle of about 75° . Moreover, the ring current topology (not the structure; see Fig. 3) appears to be unchanged compared to the 90° case. It is tempting to speculate that the ring current topology does not change until a certain limiting angle is reached. For small angular changes this is intuitively evident.

Based on these observations on the dependence of electron delocalization, relative orientation of the magnetic field and the resulting ring current structures, a conjugated polyene was constructed with a carbon atom backbone following the course of \mathbf{j} displayed in Fig. 1(c). To minimize ring strain, a large molecule of the formula $\text{C}_{144}\text{H}_{144}$ was chosen (1, see Fig. 4). A geometry optimization indicated that the molecule is highly symmetrical (point group D_{18} with only four non-equivalent H and C atoms, respectively). A subsequent symmetry-restricted optimization and frequency analysis has confirmed this. Compound 1 is a cyclic oligo-acetylene. The energy of formation amounts to 39 kcal per mol of acetylene. Its primary structure is that of a conjugated polyene with shorter and longer alternating bonds starting from the bonds close to the center of symmetry to the outer parts of the molecule: 1.420, 1.382, 1.420, 1.386, 1.422, und 1.386 Å. Moreover, there is an all-*cis* connectivity of all carbon atoms causing a helical *cis-cisoid* secondary structure. Helical polyacetylenes with an all-*cis-cisoid* conformation have been known for some time. Recently they have come into the focus of materials research, where

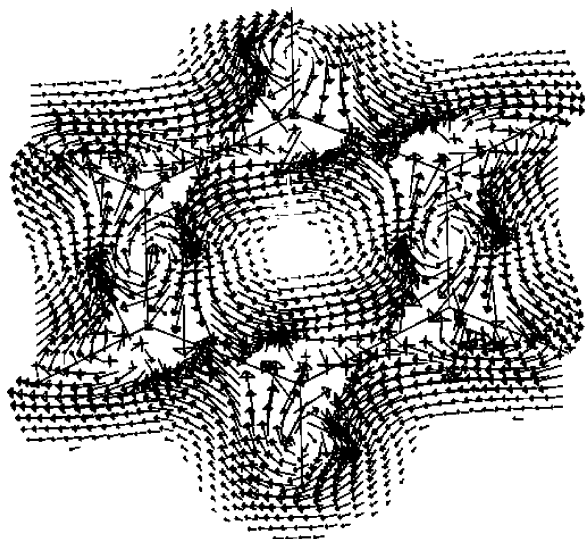


Fig. 3. The molecular plane and the external magnetic field (**B**) are forming an angle of 45° (as in Fig. 2). The arrows shown are magnetically induced current density vectors in the molecular plane. A comparison with Fig. 2(a) from reference [1] leads to the assumption that the ring current topology (or more precisely, the topology of the stagnation graph) is within certain limits independent of the relative orientation of the magnetic field and the molecule.

they are used as precursors for structured materials like “helical graphite” [16]. In contrast to non-cyclic helical polyacetylenes, **1** does not exhibit a linear tertiary structure, and also the periodicity of the helices is different. In **1**, there are repeating units of eighteen C_8H_8 subunits, while according to the geometry optimization, the open-chain derivative $H(C_{144}H_{144})H$ (**2**) shows a periodicity between 8 and 9 (no small integer periodicity can be assigned). The calculations show that the hydrogenation reaction of **1** leading to **2** releases 19 kcal of energy per mol of C_8H_8 . This hints at a pronouncedly strained ring system. Technically, **1** is a $4n$ π -electron system ($n = 18$), with an a_1 -type HOMO and an a_2 LUMO. The HOMO-LUMO energy gap is 0.48 eV. The four lowest symmetry-allowed electronic transitions from the ground state are at 205 and 120 nm (e_1) with much weaker transitions at 336 and 142 nm (a_2). However, it must be assumed that there are many excitation paths due to a wealth of possible low-frequency rovibronic couplings. Eighty normal modes with vibrational frequencies below 100 cm^{-1} , with the lowest at 3 cm^{-1} (Raman active), have been calculated. The lowest IR-

active mode is at 13 cm^{-1} , corresponding to a rolling motion of the whole molecule up and down the main axis of symmetry (transformed to a fixed center of mass). Such very low eigenfrequencies are not unexpected for a closed loop “molecular spring” with a large circumference and are not necessarily connected with structural instabilities.

Due to the high symmetry of **1** and the propensity of the employed quantum chemistry program (TURBOMOLE, see Computational Details) to account for high-order axis of symmetry, it was also possible to calculate magneto-chemical properties of this macromolecule. Both the 1H and ^{13}C nuclear-magnetic-resonance (NMR) chemical shifts are distributed within the typical aromatic region, with a clear downfield trend from the outer rim ($-x$, $-y$ direction) of the molecule to the center-oriented inner rim [1H NMR: δ (rel. TMS) = 5.9, 5.9, 6.5, and 7.7 ppm; ^{13}C NMR: δ (rel. TMS) = 129.6, 133.8, 138.4, and 148.5 ppm]. This is in agreement with the proposal that the induced diamagnetic currents follow the carbon atom backbone, while the H atoms, which are outside the backbone, are downfield shifted in analogy to the situation in benzene. The upfield shift tendency within these atoms (7.7 to 5.9 ppm and 148.5 to 129.6 ppm), when going from atoms close to the molecular center to the outside (x , y direction), can be explained by the increasing C–C–C–C dihedral angles in the outer region. This leads to a weakening of the π overlap and to less electron delocalization and consequently to smaller induced currents.

To demonstrate the anapole character of **j** in **1** in a perpendicular magnetic field, some induced-current vectors on a toroid surface with a small diameter of 1 Å inside the molecule can be considered. The current vectors wind around the torus [Fig. 4(b)] in a way similar to the situation shown in Fig. 1(c). The total induced current flowing through the molecule amounts to 16 nA T^{-1} (30 nA T^{-1} is the diamagnetic and -14 nA T^{-1} is the paramagnetic contribution thereof). These values are more than one and a half times those which are found in benzene. The innermost current vortex flowing around the center of the molecule is paratropic. In this respect the ring current topology is similar to what is found in other cyclic planar aromatic molecules [9, 10].

In the quest to find other possible representatives of this newly proposed class of compounds, it turns out that an analogous species with the molecular for-

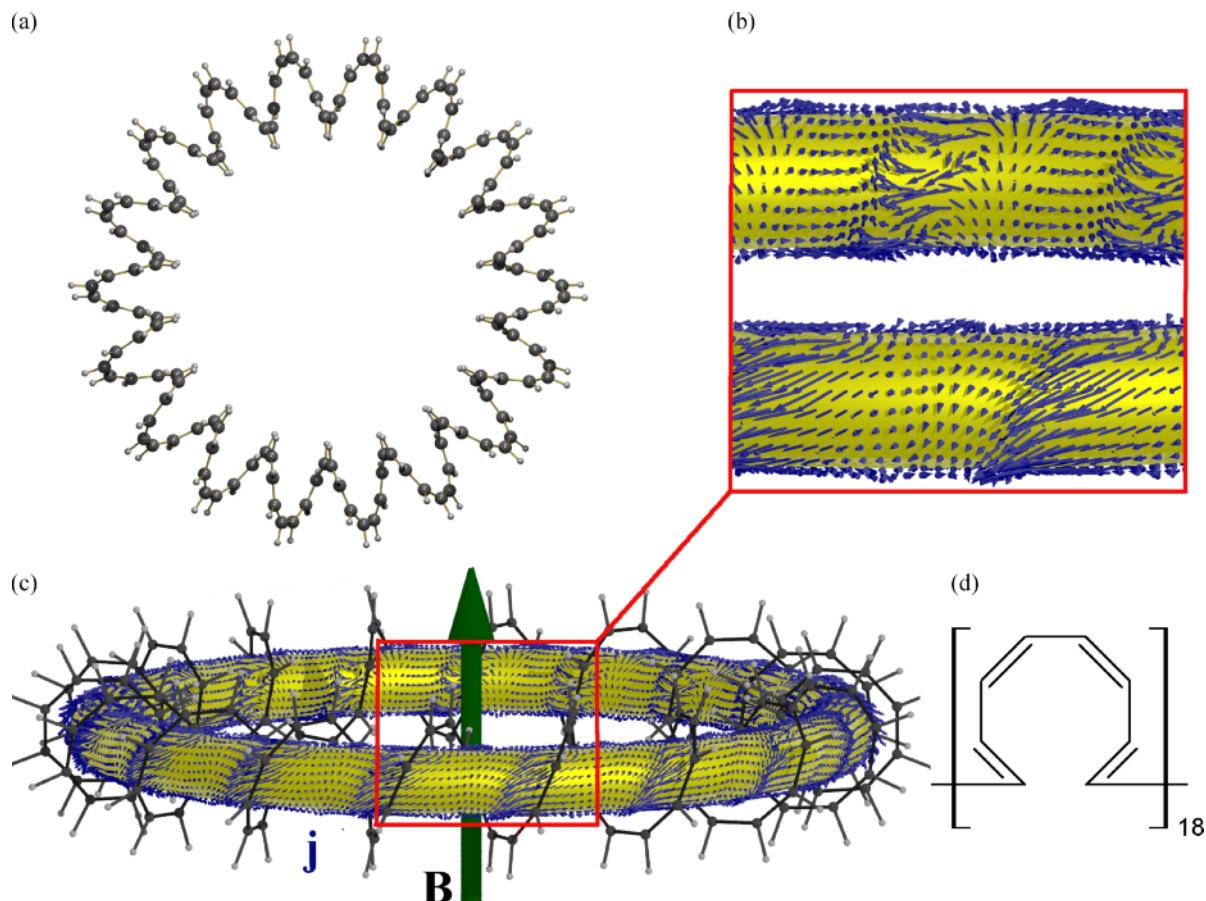


Fig. 4 (color online). (a) Optimized structure of **1**; (b) ring current detail from (c); (c) side-view of **1** with calculated current density vectors (blue) on a toroid surface (gold), induced by a weak external magnetic field **B** (green arrow); (d) molecular formula of **1**.

mula $(C_6H_6)_{18}$ with six-fold periodicity does not display a minimum on the potential hyper-surface. Further investigations in our and other laboratories are being made.

Computational Details

The structures of **1** and **2** were optimized with the TURBOMOLE program package (version 6.2) [17]. DFT with the BP86 energy functional and in the RI approximation was used throughout [18]. All calculations [including the “lowest eigenvalue search” (LES) for the verification of the minimum structure] were performed using the comparably large def2-TZVP [19] basis set on carbon and hydrogen atoms, and under D_{18} symmetry. This combi-

nation of method and basis set is known to work reliably for the calculation of the energy and the ground state structure of purely organic closed-shell molecules consisting of only first and second row elements and in absence of significant dispersion-type interactions.

A full frequency analysis was carried out with the def2-SV(P) basis set [17] for the corresponding equilibrium structure of **1**. In all calculations the m4-type integration grid was employed, and further non-standard settings used were \$scfconv = 8 and \$denconv = 0.1d-06. The chemical shielding tensors and the corresponding electron density matrices were calculated without the RI approximation using TURBOMOLE’s module mpshift. Six electronic excitations (a_2 and e_1 , respectively) were calculated using the TD-

DFT approach as it is implemented in TURBOMOLE's egrad module. The magnetically induced current density vectors and the current integrations were done with GIMIC (version 1.4) [20].

Coordinate files with cartesian coordinates of **1** in Å at the RI-DFT(BP86)/def2-SV(P) and at the RI-DFT(BP86)/def2-TZVP levels of theory are supplied as Supporting Information (online only). These coordinates can be read in from a file "coord" (the supplied files have to be renamed accordingly) into TURBOMOLE's define module using the command "aa coord".

The remaining 280 symmetry-dependent sites can be generated with the command "sy d18".

Supporting information

A coordinate file (B12189-suppmat1-coord1.txt) with cartesian coordinates of **1** in Å at the RI-DFT(BP86)/def2-SV(P) level of theory and a coordinate file (B12189-suppmat1-coord2.txt) with cartesian coordinates of **1** in Å at the RI-DFT(BP86)/def2-TZVP level of theory are supplied as Supporting Information available online (DOI: [10.5560/ZNB.2012-0189](https://doi.org/10.5560/ZNB.2012-0189)).

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