Quantification of molecular aromaticity as a predictive factor of astrophysical significance

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\textbf{ABSTRACT}

\textit{Context.} This study reports the index of aromaticity calculated by numerical integration of the magnetically-induced current density for cyclic hydrocarbon molecules both known to exist in astrophysical media as well as those proposed to exist.

\textit{Aims.} This study promotes the ring current strength (RCS) value for quantifying aromaticity as a means of predicting astrophysical detectability.

\textit{Methods.} Density functional theory (DFT) calculations at the B3LYP/aug-cc-pVTZ level provide optimized structures and the wavefunctions needed to provide the RCS values for the molecules analyzed.

\textit{Results.} The known interstellar molecules examined \(-\text{C}_3\text{H}_2\), \(-\text{C}_3\text{H}_2\text{C}_3\), \(-\text{C}_4\text{H}_2\text{H}_{\text{C}}\), \(-\text{HCNN}\), \(-\text{HCNN}^+\), \(-\text{HCNN}^+\) \(\text{CN}\) \(\text{O}\text{C}_{\text{H}}\text{H}_{\text{O}}\), \(-\text{HCNN}^+\) \(\text{CN}\) have RCS values of less than 0.0 nA T\(^{-1}\) as expected. Several proposed interstellar molecules likely will not persist if they form due to low RCS values including \(-\text{C}_3\text{C}_2\text{H}_2\). Other species such as \(-\text{p}-\text{benzene}\) and \(-\text{HCNN}^+\) have high RCS values of 19.9 nA T\(^{-1}\) and 14.4 nA T\(^{-1}\), respectively.

\textit{Conclusions.} Cyclic hydrocarbons previously observed in astrophysical media have high RCS values. Those with low or negative RCS values have yet to be observed implying that such a metric can indicate astrophysical significance.

\textbf{Key words.} astrochemistry – molecular processes – ISM: molecules – infrared: ISM

1. Introduction

The detection and study of molecules in the interstellar medium (ISM) is the core of astrochemistry. This chemical inventory helps to understand the chemical composition, formation, and evolution of the Universe. Most of the molecules detected thus far are acyclic and carbon-based. Nevertheless, cyclic and aromatic molecules have also now been detected after having been theorized for decades. Their formation mechanisms, stabilities, and lifetimes under extreme conditions in the ISM are not fully understood, but ongoing work is continually providing new insights (Allamandola 2011; Allamandola et al. 1989).

One of the first cyclic molecules detected in the ISM was cyclopropenylidene, \(-\text{C}_3\text{H}_2\) (Thaddeus et al. 1985) preceded by \(-\text{C}_3\text{SiC}_2\) the year before (Thaddeus et al. 1984). This terrestrially highly reactive hydrocarbon has been found toward a variety of astrochemical sources ranging from dense clouds to diffuse media, showing an actually high structural stability in astrochemical environments (Oike et al. 2004). Its stability can be simply explained by its \(\pi\)-aromaticity. Hückel’s \(4n + 2\) rule (Hückel 1931a,b, 1932) applies since this monocyclic, planar molecule possesses two delocalized \(\pi\) electrons giving \(n = 0\) in this system. If the simplest, cyclic, aromatic hydrocarbon is abundant in a wide swath of astrophysical regions, it stands to reason that related and/or bigger aromatic hydrocarbons should be, as well (Tielens 2008, 2013; Ge et al. 2020; Allamandola et al. 1989) an idea established years ago by Allamandola et al. (1989). These authors also point out remarkable evidence that planar organic molecules, polycyclic aromatic hydrocarbons (PAHs), are extremely stable. They stated that PAH structures are made up of fused six-membered benzene rings. Through these findings today it is well-known that a significant fraction (up to 20\%) of carbon-based molecules in the ISM exist in the form of PAHs (Allamandola et al. 1989). From these contributions the well-known term “aromatic universe” was coined, which is used by some researchers (e.g., Kaiser & Hansen 2021) to emphasize the ubiquitous nature of PAHs in the ISM, as Allamandola et al. (1989).

Following Hückel’s \(4n + 2\) rule for \(n = 1\) most readily leads to benzene as the next logical cyclic aromatic hydrocarbon. Fusing benzene rings together creates PAHs where larger numbers of delocalized \(\pi\) electrons enhance the stability of the overall molecular structure (Allamandola et al. 1989). The detection of benzene, this classic reference aromatic molecule, was first reported by Cernicharo et al. (2001) as a result of analyzing observed infrared bands in the direction of the proto-planetary nebula CRL 618s. While this detection is still not fully accepted in all astrochemical circles, the recent radio line detections of cyanobenzene (benzonitrile), \(-\text{C}_3\text{H}_2\text{CN}\) (McGuire et al. 2018), considered to be a precursor of more complex PAHs (McCarthy & McGuire 2021), together with its CN-substituted derivatives (1-cyanonaphthalene and 2-cyanonaphthalene) observed in the...
Taurus Molecular Cloud (TMC-1) (McGuire et al. 2021) provide the strongest evidence to date for the theorized ubiquity of aromatic molecules, PAHs in particular, in the ISM (Allamandola et al. 1989). This leads to the question of what other aromatic molecules can exist in molecular clouds, and if there is there an interplay between small aromatics and much larger PAHs present in different evolutionary stages of various stellar sources. The answers to these and related questions can also support the hypothesis that PAHs and their derivatives are responsible for currently unassigned astronomical spectral features, including the unidentified infrared (UIR) emission bands (Peeters et al. 2004; Sundararajan et al. 2018; Allamandola et al. 1989) that are mostly consistent with PAH signals in the mid-IR (3–13 μm).

The importance of the chemical and physical roles that aromaticity plays in the ISM is related to the stability. Thus, aromaticity may help predict the stability and lifetimes of unknown species not readily found on Earth. An important example is cyclopropenylidene itself. Under terrestrial conditions, this aromatic carbene is highly reactive, but the more diffuse media present in astrophysical environments greatly increases its lifetime (Madden et al. 1989). The stability of the structure in the presence of energetic photons is almost exclusively attributed to its aromaticity (Lee et al. 1985) implying that aromaticity may be a driving force behind the types of molecules that play an outsized role in astrochemistry.

The concept of aromaticity has been given a variety of definitions (McNaught & Wilkinson 1997). While the simplest electron-count rule of Hückel aromaticity (defined above) can fail in some special cases (Klein et al. 2021), for benzene-like molecules, the idea of a delocalized π system with electron density above and below the molecular ring with the various levels in constructive resonance suffices to determine the aromatic character of the system. Recently, Fortenberry et al. (2018) have explored a simple method for identifying aromaticity in hydrocarbons based on averaged C–C bond lengths that serves as a first-order approach to determine the aromatic character. While this provides a convenient heuristic for examining aromaticity, it fails to capture all of the nuances of this central chemical principle to the same degree as more advanced methods.

Aromaticity is often theoretically investigated through the popular nucleus-independent chemical shifts (NICS) method (Schleyer et al. 1996; Chen et al. 2005). This computational method is based on the application of an external magnetic field that induces an electron current in aromatic rings. This current, in turn, induces a secondary magnetic field allowing for the computation of isotropic magnetic shielding (NICS values) at conveniently chosen points in space, usually at the ring center or at 1.0 Å above the center of molecular ring. However, NICS values must be used with care for the assessment of aromaticity since NICS information can sometimes be unreliable (Faglioni et al. 2005; Wannere et al. 2005; Islas et al. 2010; Van Damme et al. 2016). A more reliable approach is the magnetically induced current density (MICD) method (Lazzaretti & Zanasi 1981a,b; Lazzaretti 2000). This magnetic criterion (Gershoni-Poranne & Stanger 2015) is rooted in the same principles as the NICS method: a perturbing magnetic field causes modifications in the motions of the electrons creating a current density around or in parts of the molecule. This idea is based on the ring current model (RCM) (Pauling 1936; Lonsdale 1937; London 1937). The induced current density is a vector field in three dimensions that can be visualized via streamline plots or evaluated numerically via ring current strength (RCS). The RCS is the integration of the current density over a plane. This net flux is then directly associated with aromaticity (Pauling 1936; Lonsdale 1937; London 1937). As a convention, positive RCS values are associated with aromaticity, whereas negative values indicate antiaromaticity.

In general, MICDs are considered highly valuable for the investigation of aromaticity over a wide range of molecular systems (Lazzaretti 2000; Gomes & Mallion 2001; Boldyrev & Wang 2005; Zubarev et al. 2008; Krygowski et al. 2014; Gershoni-Poranne & Stanger 2015; Merino et al. 2004; Sundholm et al. 2016b; Monaco & Zanasi 2016). In this work, we propose the use of MICDs from two points of view: a qualitative one (streamline plots) and a quantitative one (RCSs). These metrics will be applied to known astronomically observed aromatic molecules as a benchmark and then extended to other systems yet to be observed in the ISM, in circumstellar media, or elsewhere in space. This will then serve as a guide to providing insights into aromatic molecules that may have astrophysical stabilities (brought about by the aromaticity) great enough to be good candidates for observation. While most PAHs are rotationally inactive, the recent launch of the James Webb Space Telescope will certainly increase the opportunity for unique PAH observation. Even so, rotational observation will still remain the major workhorse for astronomical molecular detection, especially since there are multiple radioastronomical observatories all over the world. Hence, many of the molecules whose aromaticity is investigated in this work will include nitrogen heteroatoms, dehydrogenation, functional groups, and other structural shifts that will allow dipole moments to be present along with the aromaticity. As a result, these predictions of aromaticity can lead the way to determining molecular targets of future radioastronomical or IR observation.

2. Computational methods

All of the structures are optimized in vacuo (implying 0K) with the NWChem package (Apré et al. 2020) using density functional theory (DFT) via the B3LYP functional (Stephens et al. 1994; Becke 1993) and the correlation-consistent, triple-ζ basis set including diffuse functions (aug-cc-pVTZ basis) (Dunning 1989; Kendall et al. 1992). Starting from the optimized geometries obtained with NWChem, the calculations of the MICDs are carried out with the DIRAC code (Bast et al. 2021) using the same functional and basis sets for the elements C, O, N, and H. In this code, the MICD is obtained through linear response of the Hartree–Fock or Kohn–Sham determinant to the perturbing external magnetic field (Bast et al. 2009). The use of London atomic orbitals (LAOs) radically minimizes the possible errors introduced by the use of finite basis sets (London 1937; Sulzer et al. 2011). All computations were carried out assuming a closed-shell singlet ground state.

In this work, visualization of the current flow plays an important role in the analysis of aromaticity. This visualization is realized by using both two-dimensional and three-dimensional streamline plots. The two-dimensional plots (current-density maps, CDMS) are qualitative streamline plots generated by “slicing” the three-dimensional MICD vector field in order to reveal complex current density patterns. The CDMS are generated using a Python script (Van Rossum & Drake 2009) and visualized with the Matplotlib package (Hunter 2007). As a convention, the clockwise (diatropic) and counterclockwise (paratropic) direction of the current flow indicates aromaticity or antiaromaticity, respectively. For simple cases, the Paraview program (Ayachit 2015) is used to visualize three-dimensional streamline plots of the current density vector field.
For the sake of a quantitative comparison between different molecules, a better aromaticity index is the net RCS (Jusélius et al. 2004; Johansson et al. 2005; Sundholm et al. 2016a). This is a measurable quantity called the integrated bond current susceptibility (or bond current strength) which accounts for the net current intensity between two bonded atoms in a molecule. The net RCS can be expressed in terms of diatropic and paratropic contributions; positive values indicate diatropic currents (clockwise direction), whereas negative values indicate paratropic currents (counterclockwise direction). A positive value of the RCS indicates aromaticity, and a negative value indicates antiaromaticity. In general, the integration plane bisects half of a bond cross section of two atoms in the molecular ring. This integration plane is chosen to be perpendicular to the molecular ring. Usually, one edge of the plane starts at the ring geometric center extending 1.0 Å above, below, and outward; in other special cases, the plane must start at a vortex center (zero flux region) within the ring since the current pathways do not always take the shape of the molecular ring. As an example, Fig. A.1 in the electronic supporting information (ESI) shows a three-dimensional representation of the integration plane for benzene. The SI unit of RCS is nA T⁻¹.

3. Results

All of the molecules considered in this work are presented in Fig. 1 and Table 1. First, the description and analysis of the aromaticity of benzene is key to understanding the entire series of molecules in this table since benzene is viewed as the quintessential aromatic molecule. The aromaticity of benzene, using the MICD method, has been extensively studied over the years (Jusélius et al. 2004; Bast et al. 2009; Lazzeretti 2000; Havenith & Fowler 2007; Torres-Vega et al. 2015; Ramirez-Tagle et al. 2004; Johansson et al. 2005; Sundholm et al. 2016a). This series of molecules in this table since benzene is viewed as the planar representation of the integration plane for benzene. The SI unit of RCS is nA T⁻¹.

Table 1. Calculated diatropic, paratropic, and net current strengths (RCSs, in nA T⁻¹) at the B3LYP/aug-cc-pVTZ level.

<table>
<thead>
<tr>
<th>Molecules</th>
<th>Diatropic</th>
<th>Paratropic</th>
<th>Net current</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>16.9</td>
<td>-5.1</td>
<td>11.8</td>
</tr>
<tr>
<td>c-C₃H₂</td>
<td>12.5</td>
<td>0.0</td>
<td>12.5</td>
</tr>
<tr>
<td>c-(C≡C)H₂</td>
<td>8.7</td>
<td>-5.3</td>
<td>3.5</td>
</tr>
<tr>
<td>c-(O)C₃H₂(a)</td>
<td>10.0</td>
<td>-6.8</td>
<td>3.2</td>
</tr>
<tr>
<td>c-C₃H₅</td>
<td>9.9</td>
<td>0.0</td>
<td>9.9</td>
</tr>
<tr>
<td>c-C₃H₅C_3</td>
<td>16.0</td>
<td>-2.4</td>
<td>13.6</td>
</tr>
<tr>
<td>c-C₃H₅CN</td>
<td>12.2</td>
<td>-0.8</td>
<td>11.4</td>
</tr>
<tr>
<td>c-N₂H₃</td>
<td>11.5</td>
<td>-0.6</td>
<td>10.9</td>
</tr>
<tr>
<td>c-HCCN</td>
<td>12.7</td>
<td>-2.2</td>
<td>10.5</td>
</tr>
<tr>
<td>c-CNC</td>
<td>13.3</td>
<td>-0.5</td>
<td>12.7</td>
</tr>
<tr>
<td>c-CNN</td>
<td>15.9</td>
<td>-3.0</td>
<td>12.9</td>
</tr>
<tr>
<td>c-HCNN*</td>
<td>14.5</td>
<td>-0.1</td>
<td>14.4</td>
</tr>
<tr>
<td>c-N</td>
<td>14.9</td>
<td>-0.7</td>
<td>14.2</td>
</tr>
<tr>
<td>c-H₃⁺</td>
<td>12.2</td>
<td>-1.6</td>
<td>10.6</td>
</tr>
<tr>
<td>c-H₃⁻</td>
<td>17.8</td>
<td>-4.6</td>
<td>13.1</td>
</tr>
<tr>
<td>c-H₃⁺</td>
<td>14.7</td>
<td>-5.5</td>
<td>9.2</td>
</tr>
<tr>
<td>c-H₄</td>
<td>2.7</td>
<td>22.7</td>
<td>-20.0</td>
</tr>
<tr>
<td>c-C₆H₆</td>
<td>8.5</td>
<td>-9.7</td>
<td>-1.3</td>
</tr>
<tr>
<td>c-C₆H₆(b)(planar)</td>
<td>2.9</td>
<td>42.9</td>
<td>-40.1</td>
</tr>
<tr>
<td>c-C₆H₆(b)(planar)</td>
<td>24.2</td>
<td>-4.1</td>
<td>20.1</td>
</tr>
<tr>
<td>c-C₆H₆CN(benzonitrile)</td>
<td>16.5</td>
<td>-5.3</td>
<td>11.2</td>
</tr>
<tr>
<td>m-benzene</td>
<td>14.9</td>
<td>5.2</td>
<td>9.7</td>
</tr>
<tr>
<td>o-benzene</td>
<td>17.5</td>
<td>-3.8</td>
<td>13.7</td>
</tr>
<tr>
<td>p-benzene</td>
<td>21.9</td>
<td>19</td>
<td>19.9</td>
</tr>
<tr>
<td>pentalene</td>
<td>5.0</td>
<td>-24.8</td>
<td>-19.8</td>
</tr>
<tr>
<td>naphthalene</td>
<td>17.8</td>
<td>-4.8</td>
<td>13.0</td>
</tr>
<tr>
<td>1-CN – naphthalene(c)</td>
<td>17.8</td>
<td>-4.7</td>
<td>13.1</td>
</tr>
<tr>
<td>2-CN – naphthalene(c)</td>
<td>17.2</td>
<td>-4.8</td>
<td>12.4</td>
</tr>
<tr>
<td>anthracene(c)</td>
<td>20.2</td>
<td>-4.4</td>
<td>15.8</td>
</tr>
<tr>
<td>pyrene(c)</td>
<td>15.9</td>
<td>-5.1</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>20.9</td>
<td>-4.4</td>
<td>16.4</td>
</tr>
</tbody>
</table>

Notes. (a) Two possible values. (b) These molecules, which are actually transition states, were forced to be planar on their potential energy surfaces. (c)Molecules with more than one symmetry-uniform ring.

However, the simplest π-aromatic compound is actually not benzene. The astronomically abundant cyclopentadiene, c-C₃H₄, actually fits the Hückel 4n + 2 rule with n = 0. While the π bonding between the two carbon atoms at the base of the triangle dominates the π electron cloud, the carbene carbon at the apex of the triangle possesses an empty p orbital where aromatic delocalization readily occurs. Cyclopentadiene shows complex sigma bonding pathways for the CDM in the molecular plane (0.00 Å in Fig. A.2) similar to benzene. However, at greater distances (like 1.0 Å utilized to produce the upper left image in Fig. 3), the dominance of diatropic currents clearly yields strong aromaticity with a RCS value of 12.5 nA T⁻¹, as shown in Table 1. Thus, c-C₃H₄ gives all indications of being even slightly more aromatic than benzene. This is not surprising given the exceptionally high abundances of this molecule supporting the hypothesis that strongly aromatic molecules will likely persist to a greater extent than other COMs in the ISM or other astrophysical environments.

For the sake of comparison, the proposed astromolecule (Agbaglo et al. 2019) cyclopentadienyl carbene c-(C≡C)H₃

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Fig. 1. Optimized cyclic molecules (at the B3LYP/aug-cc-pVTZ level) considered in this work. Spheres in gray, light gray, blue, and red represent C, H, N, and O, respectively. The molecules flagged with (*) are forced to be planar, but are actually transition states on their potential energy surface.

(cyclopropenylidene with an additional carbon atom bonded to the apical carbon; see Fig. 3) exhibits a CDM that has a distorted current flow around the triangular ring. On the other hand, the CDM reveals a strong counterclockwise (paratropic) flow around the external carbon atom not in the ring. The RCS value of 3.5 nA T$^{-1}$ indicates partial or weak aromaticity in line with previous work (Wang et al. 2010). In $c$-$C_3H_2$ the paratropic contribution is zero, whereas in $c$-$(C)C_3H_2$ the paratropic
Conversely, cyclopropenone c-(O)C\(_2\)H\(_2\) (cyclopropenylidene) with an oxygen atom bonded to the apical carbon instead of a carbon atom; see Fig. 3), astrophysically detected by Hollis et al. (2006), reveals a strong clockwise (diatropic) flow around the oxygen atom in its CDMs. By placing the edge of the integration plane at the center of the internal vortex (Fig. 3), the calculated RCS value is 3.2 nA T\(^{-1}\). However, a careful examination of the CDM reveals that the current flow does not include the apical carbon atom, and therefore this atom does not contribute to the net RCS, even though it should. Thus, this value could be considered ambiguous. On the other hand, if the integration plane starts downward at the external vortex (outside the C\(_3\) ring), the RCS is much more in line with what is expected of aromatic interstellar species at 9.9 nA T\(^{-1}\). While this is less than benzene, a reduction of less than 20% in the RCS value still implies a sufficient level of aromaticity. Since this molecule is known in space, RCS values of around 10 nA T\(^{-1}\) at least imply enough stability to be observed

Functionalization of the cyclopropenylidene on carbon atoms in addition to the carbene carbon shifts the RCS values to even stronger aromaticity than c-C\(_2\)H\(_2\). The first astronomical detection of ethynyl cyclopropenylidene (c-C\(_3\)HC\(_2\)H) was recently reported in TMC-1, and its formation in space is most likely due to the reaction of the CCH radical and the abundant c-C\(_2\)H\(_2\) molecule (Cernicharo et al. 2021a; Fortenberry 2021). However, laboratory and computational studies showed a year earlier, that this molecule can indeed be formed through the bimolecular gas-phase reaction of methylidyne radical CH with diacetylene HCCCCH (He et al. 2020). The CDMs of c-C\(_3\)HC\(_2\)H show a complex current flow within the small C\(_3\) ring. The strongest flow of current involves the C\(_3\)H moiety with a net RCS of 13.6 nA T\(^{-1}\). This flow of current is mostly due to the current density near the molecule plane; this is evident by examining the CDMs at 0.5\(\alpha_0\) and 1.0\(\alpha_0\). This high level of \(\pi\)-aromaticity supports the case that the ethynyl functionalization slightly adds to the stability of c-C\(_3\)HC\(_2\)H, further supporting the hypothesis that strong aromaticity helps molecules survive astrophysical conditions.

Changing the functionalization from ethynyl to the iso-electronic cyanogen group changes the aromaticity, but only to a small degree. The cyanocyclopropenylidene c-C\(_3\)HCN, first studied in depth in the laboratory by McCarthy et al. (1999), expresses current pathways similar to those of the isoelectronic c-C\(_3\)HC\(_2\)H, but with a reduced net RCS of 11.4 nA T\(^{-1}\) compared to c-C\(_3\)HC\(_2\)H and even c-C\(_2\)H\(_3\). This reduction is a consequence of the electron-withdrawing cyano group that reduces stability within the ring. While c-C\(_3\)HCN has yet to be observed with only upper limit abundances established (Cernicharo et al. 2021a), its interstellar abundance or lifetime may be less than c-C\(_3\)HC\(_2\)H since its aromaticity is lower than the ethynyl-substituted version.

Continuing with the modifications to the cyclopropenylidene motif, the azirinyl cation (c-C\(_3\)NH\(_2^+\)) has been an interesting target for astronomical detection due to its structural relationship to cyclopropenylidene and its relatively large 2.8 D dipole moment (Bera et al. 2020). Sophisticated quantum chemical calculations have already provided its vibrational spectrum and spectroscopic constants (Kokkila Schumacher et al. 2016; Bera et al. 2020), and these should aid in future experimental high-resolution spectroscopic characterization. The presence of the N atom in the triangular ring distorts the symmetry of the current pathways in the aromaticity computations here such that most of the current density flows around the N heteroatom. For this reason, the edge of the integration plane is put on a vortex near the

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**Fig. 2.** Visualization of the current density maps (or flow) to analyze aromaticity. This visualization is realized using both two-dimensional and three-dimensional streamline plots. The clockwise (diatropic) and counterclockwise (paratropic) direction of the current flow indicates aromaticity or antiaromaticity, respectively. Top: Current density maps (C at the molecular plane and at 1\(\alpha_0\) (1 bohr) distance from the plane of the benzene ring). The current flow is represented by streamlines; the magnitudes of the currents are indicated by a decreasing scale: white-yellow-red-black. Middle and bottom: Two orientations of the three-dimensional current density vector field.

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Contribution is \(-5.3\) nA T\(^{-1}\), thus drastically reducing the net RCS. The extra carbon atom in c-(C)C\(_2\)H\(_2\) distorts the \(\pi\) cloud in this molecule and reduces the aromaticity of the C\(_3\) ring (Wang et al. 2010). While the unsaturated bonding and pair of C=C \(\pm\) C=C stretching frequencies are reminiscent of PAH frequencies (Agbaglo et al. 2019), the aromaticity does not share the same correlation, which suggests that c-(C)C\(_2\)H\(_2\) may not be nearly as abundant as its molecular parent of cyclopropenylidene.
Fig. 3. Current density maps (CMDs) at 1\textit{a}_0 (1 bohr) distance from the plane of the ring for selected molecules in Table 1. The current densities are represented by streamlines; the magnitudes of the current density are indicated by a decreasing scale: white-yellow-red-black. The external magnetic field vector points toward the reader. The position of the integration plane is indicated by a line labeled with the calculated net RCS (in units of nA T^{-1}).
C-C bond (Fig. 3) in order to obtain a reliable RCS value of 10.9 nA T\(^{-1}\). While this value is lower than that of c-C\(_2\)H\(_4\) itself as well as benzene, it remains in the aromatic range above that of c-(O)C\(_2\)H\(_3\). However, this reduction in aromaticity brought about by the N heteroatom likely reduces its stability and astrophysical persistence compared to the other molecules.

A case in point is c-HCCN, which is again similar in construction to cyclopropenylidene, but with a 10.5 nA T\(^{-1}\) net RCS value. However, the quasi-linear triplet form of HCCN is now on the roster of known astronomical molecules with its detection reported by Guelin & Cernicharo (1991), implying that the c-HCCN form may also be a viable molecule for astronomical detection. In order to build the spectral database for this molecule and to observe c-HCCN, theoretical studies have been performed to analyze and describe the spectroscopy (Inostroza et al. 2013) and the structural stability of this molecule together with its relevant and stable isomers (Inostroza et al. 2011) including the linear triplet, c-HCCN together with c-C\(_2\)N\(_2\), c-CNN, c-HCCN\(_n\), and c-N\(_2\). We continue our analysis of nitrogen-substituted cyclopropenylidene-like species. They all exhibit triangular-shaped ring pathways (Figs. 3 and A.2) formed by carbon and nitrogen atoms. However, the closed-shell nature of these structures, whose spectral properties have also been computed (Fortenberry et al. 2017), produce more aromatic stability than the c-HCCN radical or c-C\(_2\)NH\(_2\) cation. Their RCSs also indicate slightly stronger \(\pi\)-aromaticity than in benzene (11.8 nA T\(^{-1}\)), ranging from 12.7 nA T\(^{-1}\) in c-C\(_2\)N\(_2\) to 14.4 nA T\(^{-1}\) in c-HCCN\(_n\), as listed in Table 1. In c-C\(_2\)N\(_2\), c-HCCN\(_n\), and c-N\(_2\) the diatropic contribution is largely dominant. Whereas in c-CNN and c-HCCN, the paratropic contribution is non-negligible.

The cyclopropenyl cation, c-C\(_2\)H\(_2\)\(^+\), is the protonated form of cyclopropenylidene, but, more importantly, theoretical studies of Lee (2014) predict that c-C\(_2\)H\(_2\)\(^+\) is the most important precursor of the ubiquitous c-C\(_2\)H\(_2\). The c-C\(_2\)H\(_2\)\(^+\) cation was first synthesized and characterized by Breslow & Groves (1970), and its theoretical vibrational spectral features (Huang et al. 2011) led to the experimental determination of its \(v_4\) antisymmetric (\(e^\prime\)) stretching frequency at 3131 cm\(^{-1}\) (Zhao et al. 2014). Although this molecule has not yet been detected in interstellar clouds, analysis of the measurements in Titan’s upper atmosphere by the Cassini spacecraft suggest the stable existence of this molecule in such an extraterrestrial environment (Ali et al. 2013). This cation may also be considered the simplest of Hückel’s aromatic molecules not only due to its \(n = 0\) value for the \(4n + 2\) rule, but also due to its high symmetry with each carbon atom being equivalent like those in benzene. The net RCS value of c-C\(_2\)H\(_2\)\(^+\) is 10.6 nA T\(^{-1}\), slightly less than benzene and c-C\(_2\)H\(_2\), but in line with c-HCCN and the isoelectronic c-C\(_2\)NH\(_2\). The CDMs (Fig. 3) reveal two strong concentric diatropic current flows, one of them surrounding the C\(_3\) ring and the other flowing around the entire molecule much similar to that in c-N\(_2\). This behavior also supports a decent level of aromaticity for this cation, further supporting its likely astrophysical presence.

In shifting away from the cyclopropenylidene family of aromatic species, the next simplest \(\pi\)-aromatic molecule using the Hückel’s \(4n + 2\) definition is c-C\(_2\)H\(_5\), where \(n = 1\), in a construction similar to benzene. For additional consideration, the cation form c-C\(_2\)H\(_2\)\(^+\) falls outside of Hückel’s \(4n + 2\) rule since this molecule has 4 \(\pi\) electrons. The current density pathways of the cyclopentadienyl molecular ions, c-C\(_2\)H\(_2\)\(^+\) and c-C\(_2\)H\(_5\), appear roughly the same (Fig. A.2), but the two extra electrons in c-C\(_2\)H\(_3\) make this molecule more aromatic than c-C\(_2\)H\(_2\). The anion’s diatropic contribution is \(-3\) nA T\(^{-1}\) larger than in the cation at 13.1 nA T\(^{-1}\), greater even than c-C\(_2\)H\(_4\) and benzene as given in Table 1. Furthermore, considering the recent detection of two cyano-derivatives of cyclopentadiene (Lee et al. 2021) followed by the detection of cyclopentadiene itself in TMC-1 (Cernicharo et al. 2021a), the detection of cyclopentadienyl-bearing molecules (Kaiser et al. 2001) appears very likely especially when coupled with the additional inherent stability given by the exposed \(\pi\)-aromaticity.

Cyclobutadiene, c-C\(_2\)H\(_4\), is considered the prototypical antiaromatic molecule (Bally 2006) with 4 \(\pi\) electrons. Unlike c-C\(_2\)H\(_2\)\(^+\) which also has 4 \(\pi\) electrons, c-C\(_2\)H\(_4\) does not have an empty \(p\) orbital in the ring that can contribute to any aromatic stability. The antiaromaticity in c-C\(_2\)H\(_4\) can be deduced, again, from Hückel’s \(4n\) \(\pi\) electron rule, but other studies based on the magnetic criterion also confirms its antiaromaticity (Fliegl et al. 2009; Pathak et al. 2013). In this study the net RCS is \(-20.0\) nA T\(^{-1}\) in agreement with previous work (Fliegl et al. 2009; Pathak et al. 2013). The corresponding CDM (Fig. 3) shows a strong dominating counterclockwise (paratropic) current flow inside the C\(_4\) ring, while a weak diatropic flow is visible around the entire molecule. Additionally, this molecule has yet to be observed in astrophysical media. This may partially have to do with its lack of a permanent dipole moment, but the antiaromatic nature of this molecule gives another indication that it will not readily arise from astrochemical hydrocarbon reactions.

Cyclooctatetraene, c-C\(_8\)H\(_8\), is also traditionally antiaromatic when planarity is forced upon it, even though the minimum is actually bent or non-planar, and it should not be present in interstellar regions. Table 1 reports its RCS value to have a much smaller magnitude than c-C\(_2\)H\(_4\) at \(-1.3\) nA T\(^{-1}\), and the negative value still communicates its antiaromatic character. Conversely, cyclodecapentene, c-C\(_{10}\)H\(_{10}\), is shown to be aromatic with a 20.1 nA T\(^{-1}\) value that is in line with \(n = 2\) in the \(4n + 2\) rule. However, both of these species are well known to be non-planar in their lowest energy configurations making both susceptible to rearrangement and reaction with ambient molecules.

The classic aromaticity of benzene is also explored here with slight changes to its structure in a manner similar to that done for cyclopropenylidene above. The first such molecule is benzonitrile, c-C\(_2\)H\(_3\)CN, but this compound has been recently detected by radioastronomical observation of its emitted hyperfine-resolved transitions from the molecular cloud TMC-1 (McGuire et al. 2018, 2021). The detection is supported by Cooke et al. (2020) who carried out experiments to suggest that benzonitrile could be a proxy for benzene in the cold conditions of the ISM, and benzene can readily react with CN to create the aromatic benzonitrile. A careful inspection of the CDMS of benzene and benzonitrile (Figs. 1 and A.1) reveals that the CN group does not seem to modify the symmetry and intensity of the current pathways involving the carbon ring significantly. The CN group appears independent and exhibits a local current flow sharing a weaker diatropic perimeter current on its own. As a result, the RCS of benzonitrile is 11.2 nA T\(^{-1}\), a value only slightly lower than that of benzene (11.8 nA T\(^{-1}\)). This aromaticity and detection of benzonitrile supports the case here that \(\pi\)-aromaticity can be used as an indicator for the likely interstellar presence of these hydrocarbons.

Benzene is a hydrocarbon ring similar to benzene but with two hydrogen atoms removed. It exists in three isomeric species with molecular formulae c-C\(_6\)H\(_6\), namely m-C\(_6\)H\(_6\) (meta-benzene), o-C\(_6\)H\(_6\) (ortho-benzene), and p-C\(_6\)H\(_6\) (para-benzene). The o-C\(_6\)H\(_6\) isomer has recently been astrophysically detected by Cernicharo et al. (2021b) in the direction of TMC-1. Hence, any signs of strong aromaticity in any of these isomers bodes well.

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for this property being an indicator of astrophysical significance. The \( C_6 \) ring in the \( o-C_6H_4 \) isomer deviates slightly from the regular, hexagonal geometry (Fig. 3) due to the triple bond \( 6 \). The \( C_p \) for this property being an indicator of astrophysical significance.

Wierschke et al. (1993). Of the three isomers, \( o-C_6H_4 \) is the most stable, followed by \( m-C_6H_4 \) and \( p-C_6H_4 \) (Olsen 1971) respectively at 13.1 and 39.2 kcal mol\(^{-1}\) higher in energy from the present B3LYP/aug-cc-pVTZ calculations.

For the present analysis the most aromatic isomer is actually \( p-C_6H_4 \) with a RCS of 19.9 nA T\(^{-1}\) (Table 1); the associated CDMs corroborate this by showing the most intense and symmetrical current pathways (Figs. 3 and A.2). The lowest aromaticity of the set, \( m-C_6H_4 \) at 9.7 nA T\(^{-1}\), makes sense if the ring distortion is considered in hindering the delocalization of the \( \pi \) electrons. However, the meta- and para-benzyne isomers are challenging problems for quantum mechanical methods because they are open-shell singlet ground state systems and require the use of a multiconfigurational theory (De Proft et al. 2002; Pathak et al. 2013; Wierschke et al. 1993). Even though the RCSs of the benzyne isomers have been determined here via a single reference method, the accurate multiconfigurational calculations reported by Pathak et al. (2013) show no striking differences between the two approaches for predicting optimized geometries and associated properties.

Moving beyond single-ring structures, compounds composed of multiple or fused aromatic rings in which the \( \pi \) electrons are delocalized certainly warrant discussion, especially for astrochemical applications. Pentacene, \( C_{20}H_{10} \), is a bicyclic 8 \( \pi \) Hückel anti-aromatic hydrocarbon (Cloke et al. 2017). The detection of pentacene in the ISM has yet to be reported, but Bouwman et al. (2016) simulated interactions between carbon-rich grains and galactic cosmic-rays using mass spectrometric and infrared spectroscopic techniques. This work suggests that the formation of the pentacene cation may be the result of a dissociative ionization of naphthalene, but the cation will have one less electron, thus creating a structure that is not clearly anti-aromatic like the neutral. The quantitative assessment of antiaromaticity in pentacene has been the subject of several studies (Sundholm et al. 2016a; Mauksh & Tsogoeva 2017; Fowler et al. 2004; Cuesta et al. 2005). Particularly, the RCS value of \( -19.9 \) nA T\(^{-1}\) reported by Sundholm et al. (2016a) is in notable agreement with the value reported in the present work \( (-19.8 \) nA T\(^{-1}\) in Table 1). Furthermore, the CDMs (Figs. 3 and A.2) reveal a strong paratropic current flow confirming the high antiaromatic character of this molecule. Hence, this strong anti-aromaticity implies that such a molecule will not be as astrochemically significant as other PAHs such as those that follow.

Naphthalene (NP), \( C_{10}H_8 \), represents the simplest PAH composed of two fused benzene rings. The lack of a permanent dipole in isolated NP precludes the observation of a pure rotational spectrum. However, Kaiser & Hansen (2021) report experimental and theoretical studies for synthetic routes leading to a viable formation of NP in the extreme environmental conditions of the ISM (Kaiser & Hansen 2021). There is also spectroscopic evidence claiming the possible presence of the naphthalene cation at the star Cernis 52 (Iglesias-Groth et al. 2008), but conclusive confirmation of this finding has failed thus far (Searles et al. 2011). However, two cyano-substituted derivatives of NP have recently been detected by McGuire et al. (2021) in TMC-1, 1-cyanonaphthalene (1-CNN) and 2-cyanonaphthalene (2-CNN). These have notable permanent dipole moments enabling the measurement and radioastronomical observation of their rotational spectra. The ring currents and aromaticity of isolated NP have been reported by several authors (Zanasi & Lazzaretti 1997; Cuesta et al. 2009; Steiner et al. 2002; Sundholm et al. 2016a). The RCS associated with an individual ring (local aromaticity) of NP is 13.0 nA T\(^{-1}\) in line with and slightly greater than benzene, and the corresponding CDM at 1.0 \( \alpha_0 \) (Fig. A.2) from the molecular plane shows a dominant diatropic current density flowing around its perimeter. The RCS values for the unsubstituted rings of 1- and 2-CNN are nearly identical at 13.1 nA T\(^{-1}\) and 12.9 nA T\(^{-1}\), respectively. Furthermore, the local RCSs of the unsubstituted benzene rings in 1-CNN and 2-CNN are essentially the same as in the isolated NP. In contrast, the RCS in the adjacent ring is quenched by \( \sim 0.7 \) nA T\(^{-1}\) caused by the presence of the CN group. Even so, there is once again high aromaticity present in known interstellar cyclic hydrocarbons.

Finally, the discovery of larger PAHs such as anthracene and pyrene is still unconfirmed, but Vijh et al. (2004) report spectral signatures associated with both molecules toward the Red Rectangle nebula. In the same line, Iglesias-Groth et al. (2010) report the discovery of a new broad band originating at the Cernis 52 star consistent with low temperature laboratory gas-phase measurements of the strongest band of the anthracene cation. In anthracene, the CDM at the molecular plane shows two diatropic vortices involving the central C–C bonds. These local bond currents rapidly fade away at greater distances from the molecular plane retaining a strong diatropic current on the periphery of the carbon framework. Clar’s \( \pi \)- sextet rule (Clar 1972) helps to explain qualitatively the current pathway patterns of the benzenoid rings in anthracene. In principle, all rings in these molecules are aromatic because of the “migrating sextet” rule, but the rule does not determine which particular ring is the most aromatic (Solà 2013). The RCS of the central ring (outer bond) in anthracene is a very strong at 15.8 nA T\(^{-1}\), which is 3.5 nA T\(^{-1}\) larger than the other two rings, but the high degree of aromaticity of the central ring has already been noted by other authors (Schleyer et al. 2001; Mattio et al. 2005). The current density patterns of pyrene (CDM at 1 \( \alpha_0 \) in Fig. A.2) seem to match the most dominant resonance form, as expected from Clar’s sextet theory (Solà 2013; Lampkin et al. 2020). In this case, the non-adjacent rings are the most aromatic with associated RCS values of 16.4 nA T\(^{-1}\), whereas each of the two adjacent rings carry a current of 10.8 nA T\(^{-1}\), a difference of 5.6 nA T\(^{-1}\). As the ring current model follows the principle of charge conservation (satisfying a continuity equation), the difference between the two cases can be explained in terms of Kirchhoff’s junction rule of electricity (Smith 1963), which states that the sum of all currents entering a node is equal to the sum of all currents leaving the node. The calculated net current (see Fig. A.3) passing between the C–C bond of two non-equivalent rings is 5.4 nA T\(^{-1}\), in very good agreement with the expected value. While neither of these PAHs has been observed in the ISM, again, strong aromaticity appears to be a strong indicator of astrophysical significance that would lead to feasible detection.

4. Conclusions

Quantifiable aromaticity may be an indicator of astrophysical detectability in cyclic hydrocarbons with \( \pi \) electron clouds. While several factors lead to the creation of any given molecule, aromaticity appears to be tied with persistence of the molecule for observation. The minimum RCS value for aromatic

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character appears to be at least 10 nA T^{-1}. The astrophysically known c-C_{4}H_{2}, c-(O)C_{6}H_{2}, c-C_{6}H_{2}CH_{2}, o-benzene, benzonitrile, and 1- and 2-CNN molecules all possess RCS values ranging from 9.9 to 13.7 nA T^{-1}. Hence, related molecular species in this range are promising targets for radioastronomical or IR observation. While the large RCS of p-benzene at 19.9 nA T^{-1} is promising, its lower stability compared with the observed o-benzene may limit its formation, but the heightened aromaticity should increase the lifetime of any higher-energy isomer that may form in similar astrophysical environments. Likewise, nitro-should increase the lifetime of any higher-energy isomer that promising, its lower stability compared with the observed o from 9.9 to 13.7 nA T^{-1}vation. While the large RCS of range are promising targets for radioastronomical or IR obser-


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Fig. A.1. Example case for the benzene molecule. The integration plane is placed at the ring center 8 or at a vortex center, and it extends 10 bohr above, below, and outward.
Fig. A.2. Current density maps on the plane of the ring (left), at 0.5$a_0$ (center), and at 1.0$a_0$ distance (in bohr) from the plane of the ring. The current densities are represented by streamlines; the magnitudes of the current density are indicated by a decreasing scale: white-yellow-black. The external magnetic field vector points toward the reader. The integration plane is perpendicular to the molecular plane and is indicated by a cyan line, labeled with the calculated net ring current strength (RCS) in nA T$^{-1}$. (continued on next page)
Fig. A.3. Ring current strengths (RCSs) of pyrene approximately obey Kirchhoff’s junction rule of electricity. The $16.4 \text{nA} \ T^{-1}$ current that enters the carbon node is approximately equal to the sum of the other two currents leaving node.