Quantification of the Helicality of Helical Molecular Orbitals

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Abstract

The frontier molecular orbital (MO) topology of linear carbon molecules, such as polyynes, can be visually identified as helices. However, there is no clear way to quantify the helical curvature of these \( \pi \)-MOs and it is thus challenging to quantify correlations between the helical curvature and molecular properties. In this paper, we develop a method that enables us to compute the helical curvature of MOs based on their nodal planes. Using this method, we define a robust way of quantifying the helical nature of MOs (helicality) by their deviation from a perfect helix. We explore several limiting cases, including polyynes, metallacumulenes, cyclic allenes, and spiroconjugated systems where the change in helical curvature is subtle, yet clearly highlighted with this method. For example, we show that strain only has a minor effect on the helicality of the frontier orbitals of cycloallenes and that the MOs of spiroconjugated systems are close to perfect helices around the spiro-carbon. Our work provides a well-defined method for assessing orbital helicality beyond visual inspection of MO isosurfaces, thus paving the way for future studies of how the helicality of \( \pi \)-MOs affects molecular properties.

Introduction

Molecular orbitals (MOs) have long been an essential tool in the toolbox of chemists. While they are not physical observables, they have nonetheless been used to develop intuition for and predict physical properties.\(^1\)\(^-\)\(^5\) Recently, the \( \pi \)-MOs of some linear carbon molecules have received increased attention due to their helical topology.\(^6\)\(^-\)\(^16\) An example of such a proclaimed helical \( \pi \)-orbital is shown in Figure 1. This is the HOMO of \( S\text{-}1,5\text{-Me}\text{-}[4]\text{cumulene} \) and it is clearly shaped like a helix. In appropriately substituted molecules, these MOs occur due to mixing of the otherwise orthogonal \( \pi \)-systems as the symmetry of the molecule is reduced.\(^14\) This helical nature of the \( \pi \)-system is a fundamental consequence of the molecular symmetry and is evident when an appropriate Hückel model is made for the symmetry-adapted MOs as shown in Figure 1b. Even at the Hückel level of theory, it is clear that the
MOs are imperfect helices as the angular steps along the molecular axis differ in magnitude. The *helicality* of the electronic structure is thus ill-defined as even the most helical cases may not be perfect cylindrical helices. In the following, we will use the term "helicality" to refer to how close an MO is to a cylindrical helix. The helicality of an MO is large if it is close to a perfect cylindrical helix.

Given the interest in helical MOs as a means to understand related properties and the range of molecular systems in which these MOs appear, it is problematic that the assessment of helical MOs relies on visual inspection alone. It is thus altogether binary; if an MO is shaped like a coil we may deem it to be helical. This definition suffices to classify the trivial example shown in Figure 1a because we can clearly see that the MO is shaped like a helix. However, we need a more stringent definition if we wish to deal with cases of varying degrees of helicality. Without a quantifiable measure of the degree of helicality of the MOs, it will not be possible to directly correlate them with observable molecular properties.

A helix is a mathematically well-defined construct. In Cartesian coordinates, a cylindrical helix, as shown in Figure 1c, is defined by the following equations:

\[
\begin{align*}
X(\phi) &= r \cos(\phi) \\
Y(\phi) &= r \sin(\phi) \\
Z(\phi) &= h \phi \\
pitch &= 2\pi h.
\end{align*}
\]  

(1)

Here, \(r\) is the radius of the helix and \(h\) is a parameter describing the vertical separation between each loop of the helix that is related to the pitch. The angle \(\phi\) is defined as shown in Figure 1c. A cylindrical helix is a curve that forms a constant angle with respect to the axis of the cylinder. Intrinsic to this definition, it has constant non-zero curvature and constant non-zero torsion. Curvature and torsion are defined by

\[
\kappa = \frac{1}{R} = \frac{r}{r^2 + h^2}.
\]  

(2)
Figure 1: Illustration of helical MOs from DFT and Hückel theory, and a cylindrical helix. (A) The highest occupied MO (HOMO) from a DFT calculation on $S$-1,5-Me-[4]cumulene. (B) Illustration of the HOMO from a Hückel calculation on [4]cumulene. On the left, each atomic orbital is plotted along the carbon chain and colored by atom site (from violet to red). On the right, a diagrammatic representation of the twist angles of the MOs projected along the z-axis. For clarity, we have only plotted the positives lobes. Adapted with permission from Garner et al.\textsuperscript{14} (C) A right-handed helix from $\phi = 0$ to $3\pi$ with $r = 1$. The mathematical definition is given beneath the plot.

Here, $R$ is the radius of curvature and $\kappa$ is the curvature. A curve with zero curvature is a straight line. The sign of $\kappa$ determines which way the helix turns with positive curvature being a right-handed ($P$) helix and negative curvature a left-handed ($M$) helix. Intuitively, curvature can be understood as to how big a cylinder the helix encloses: large curvature translates to a cylinder with a small radius. The torsion of the helix, $\tau$, is defined as

$$\tau = \frac{h^2}{r^2 + h^2}. \quad (3)$$

Positive $\tau$ gives a helix with twist up the z-axis while negative $\tau$ gives twist down the z-axis. Torsion can intuitively be understood as to how drawn out or compressed the helix is. A
helix with high torsion will have a large pitch so that a large increase in \( z \) occurs when a full turn is completed. A helix with no torsion will be a circle with curvature of \( 1/r \). It is thus possible to define objects with perfect helicality (perfect helices) and use this for assessing the helicality of less helical objects. We refer to O’Neill for a more general mathematical derivation.\(^{32}\)

In this work, we define a mathematically rigid method for assessing how helical an MO is. We use this method, which we will refer to as the Quantification of Helicality (QoH) method, to assess several limiting cases in the form of substituted \([n]\)cumulenes, polyynes, metallacumulenes, and spiroconjugated molecules. The article proceeds as follows. We go through four different examples that showcase the diversity of systems where helical MOs arise. First, we reassess \( S\)-1,9-Me-\([8]\)cumulene and 1,1-Me-\([8]\)cumulene where the MO helicality is visually apparent. Next, we show examples where the helicality of the HOMO changes when the end-groups of 1,4-diphenylidyne and \textit{trans}-1,6-Me-\([5]\)cumulene are twisted. We examine the helical MOs in \textit{trans}-\[\text{EtC}=\!(\text{C}=\!)_4\text{C}=\!\text{Ru}=\!(\text{C}=\!)_4\text{CMe}\]\(^{2+}\), a metallacumulene with a ruthenium atom in between two cumulenylidene ligands. After that, we go through the MOs of spiropentadiene and spirononatetraene, a slightly different class of compounds compared with cumulenes that still exhibit helical MOs. Finally, we assess the MOs in cycloallenes with a ring size of up to 9. Our analysis of these systems establish the varying degrees of helicality that is not apparent from a visual inspection of the MOs.

**Methods**

Molecules were optimized in the gas phase using Gaussian16 with density functional theory (DFT) using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.\(^{33}\) The 6-311G(d,p) basis set was used for all atoms. The optimization threshold was set to \textit{tight} and an \textit{ultrafine} integral grid was used. MOs are plotted at an isosurface value of 0.02 unless otherwise noted. For the metallacumulene, we used cc-pVTZ basis set for C, H and P\(^{34,35}\).
atoms and SDD basis set and effective core potential for the Ru atom.\textsuperscript{36}

To quantify how helical an MO is, we first need to define the component of the MO that we want to consider. A helical MO has two defining characteristics: Its nodal plane propagates helically through space and so will any choice of isovalue (a specific value of the wavefunction amplitude).\textsuperscript{14} While this allows for two different approaches for defining helicality, we choose the spatial propagation of the nodal plane along the molecular axis. In the supporting information (SI), we provide a description of how to evaluate an MO on a real-space 3D grid. We also provide another way of quantifying helicality by fitting the equation for a helix to the highest isovalue along the carbon-chain. We use the spatial propagation of the nodal plane in the following because it is conceptually simpler and more robust in less well-defined helical systems.

Figure 2: Four different xy-slices of the HOMO of $S$-$1,5$-$\text{Me}$-$[4]$ cumulene. (top) HOMO of $S$-$1,5$-$\text{Me}$-$[4]$ cumulene with colored lines showing the locations where the slices in the bottom are extracted from. (bottom) Slices in the xy-plane (z-axis along carbon chain) of the HOMO shown at the top. The size of each dot corresponds to the MO amplitude at each point in space, while red and blue denotes the sign (red: positive, blue: negative). The black line is a fitted, straight line through the points where the MO changes sign. The procedure is explained in-depth in the Supporting Information.
We slice the MO into xy-planes along the z-axis (the molecular axis of the carbon chain). For each slice, we only keep a subset of MO amplitude data points by filtering out any point that lies more than \( x \) Å away from \((0,0)\). In most cases, reasonable choices of \( x \) lie between 0.5 Å to 1.0 Å. After filtering, we locate all the places where the MO amplitude changes sign, i.e., we find the \( \pi \)-nodal plane. This gives two lists of points: one with points found before reaching zero (list \( A \)) and one with points found after a zero (list \( B \)). A new set of points is calculated (list \( C \)) as the midpoint between the corresponding points in \( A \) and \( B \). \( C \) thus contains the approximated points in space where the MO phase changes. The points of \( C \) are then fitted to a straight line where the offset has been fixed to 0. This is the black line seen in the four panels of Figure 2. This black line is a systematic representation of the \( \pi \) nodal plane in each slice, which we can use to visualize the nodal plane of a given MO. We can determine the angle between two subsequent slices by using \texttt{arctan2} as defined in NumPy\textsuperscript{37}. We use this to measure the angular propagation of the MO nodal plane through the molecule. By taking the cumulated sum of all the angles in \( C \), we can compare the helicality of MOs in different molecules quantitatively.

In the introduction, we defined a cylindrical helix as a curve that forms a constant angle with respect to the axis of a cylinder. A constant increase in twist between successive slices of the nodal plane is thus the principal defining feature of a cylindrical helix. From this, we expect that the cumulated sum of the angles between successive slices will be a straight line. Any deviation from a straight line indicates deviation from a perfect helix. By quantifying how much a straight line fit deviates from the cumulated sum of angles, we can find how much the MO deviates from a perfect helix. As a quantitative summary of how much a given MO deviate from a perfect helix, we report the mean absolute deviation (MAD). A higher MAD indicates deviation from a perfect helix and a lower MAD indicates that the MO is closer to a perfect helix. This deviation thus provides a rigid measure of the helicality. The MAD is given by

\[
MAD = \frac{1}{n} \sum_{i=1}^{n} |y_i - f_i|,
\]
where \( n \) is the number of data points, \( y_i \) is each observed data point, and \( f_i \) is each data point predicted by the fitted straight line.

**Results**

Substituted odd-carbon cumulenes constitute the clearest example of the difference between helical and rectilinear \( \pi \)-MOs in linear molecules. To provide examples of the potential of the QoH method, we start by revisiting longer cases than those discussed in the introduction. Shown in Figure 3, we assess the HOMO of achiral 1,1-Me-[8]cumulene and chiral \( S \)-1,9-Me-[8]cumulene. The former is a clear case of a rectilinear HOMO, and the latter of a helical HOMO. In the graph of the cumulated sum, we see that the rectilinear HOMO of 1,1-Me-[8]cumulene increases with a series of steps. Its cumulated sum of the twist does not change at all for the first \( \sim 2 \) Å and then makes an abrupt jump of \( \pi \) rad (180°) when there is a node in the MO. The HOMO of \( S \)-1,9-Me-[8]cumulene has an almost constant increase in the cumulated sum and, as explained in Methods, this is one of the defining features of a cylindrical helix. The MAD for the helical MO is 4, which gives an indication of a "low" value that suggests an almost perfect helix. In comparison, the MAD of the rectilinear HOMO of 1,1-Me-[8]cumulene is 51.

The MAD captures what we intuitively expect from a visual inspection of the isosurfaces: the HOMO is a cylindrical helix in one case, and non-helical in the other. It is worth noting here that the MAD has no upper limit for the rectilinear HOMO. Only the case of a perfect cylindrical helix is well-defined by this method, and the rectilinear shape of an MO is thus a case that is classified as *not* a cylindrical helix.

The QoH method also allows us to carry out the analysis using the Hückel model of an [8]cumulene where the appropriate \( C_2 \)-symmetry has been enforced (see SI). As is clear from Figure 3, there is good correspondence between the results from the Hückel model and the helical MO of \( S \)-1,9-Me-[8]cumulene found using DFT. In the Hückel model, there is
again a slight deviation from perfect helicality with a MAD of 3. For the Hückel model, there
are only nine sites, one for each carbon atom. This means that we only have nine data points
in the graph of Figure 3 whereas the DFT-MOs are evaluated on a near-continuous 3D-grid.
The agreement found here between Hückel theory and higher-level calculations shows the
underlying commonalities in these two descriptions of the $\pi$-MOs. In the remaining sections,
we will focus on assessing molecules where the orbital helicality is less clear than in this
initial example.

Figure 3: Change in helicity for three different systems. (top) Chemical structures and
HOMO of 1,1-Me-[8]cumulene and S-1,9-Me-[8]cumulene, respectively. (bottom) The cus-
mulated sum of the twist of the HOMO plotted against length along the cumulenic axis of
the Hückel method, 1,1-Me-[8]cumulene, and S-1,9-Me-[8]cumulene. The black, filled circles
indicate the position of the carbon atoms along the carbon chain of S-1,9-Me-[8]cumulene
and the black, dashed line is a guide to the eye. The carbon positions of both systems are
nearly identical therefore only one carbon chain is depicted. Isovalue 0.01 a.u.

Polyyynes

Polyyynes are linear chains of $sp$-hybridized carbon that can exhibit helical MOs visually simi-
lar to those seen in $\alpha,\omega$-substituted even $[n]$cumulenes.$^{10–12,19,20,25,26}$ Similarly, odd $[n]$cumulenes
can also exhibit helical MOs when the end-groups are rotated away from a co-planar orien-
tation as we show at the top of Figure 4. There is almost free rotation for the end-groups
of polyynes with the ground-state orientation determined by the type of end-groups.\textsuperscript{38–41} The ground state of odd $[n]$cumulenes is the coplanar geometry and there are considerable barriers to torsion.\textsuperscript{26,42–46} Because the ground state for both molecules converges to coplanar end-groups, all MOs for structures with a dihedral angle $> 0^\circ$ are single-point calculations where the dihedral angle has been set manually with the remaining internal degrees of freedom frozen. Note that to avoid confusion, we systematically use degrees for the torsion angles of the end-groups, whereas radians are used to denote the helical twist of the MOs.

Figure 4: Change of the HOMO of diphenyl-diyne and $trans$-1,6-Me-$[5]$cumulene with increasing torsion angle. (A) HOMO of diphenyl-diyne at $0^\circ$, $45^\circ$, and approximately $90^\circ$ dihedral angles. Note that the dihedral angle in the final is calculated at $89.5^\circ$ to break the symmetry. (B) HOMO (first three) and LUMO (last three) of $trans$-1,6-Me-$[5]$cumulene at $0^\circ$, $4^\circ$, $84^\circ$, $96^\circ$, $176^\circ$ and $180^\circ$ dihedral angles. (C) The cumulated sum of the twist of the HOMO of diphenyl-diene plotted against length along the polyynic axis at different dihedral angles. (D) The cumulated sum of the twist of the HOMO of $trans$-1,6-Me-$[5]$cumulene plotted against length along the cumulenic axis at different dihedral angles. Below each plot, the MAD is plotted for a straight line fit through the cumulated sum of angles at each dihedral angle. The filled circles indicate the position of the carbon atoms along the carbon chain. Isovalue: 0.01 a.u.

Starting with the diphenyl-diyne, at the top-left of Figure 4, we show its HOMO at three different dihedral angles of the end-groups. For the molecule to retain $C_2$-symmetry, the final step of twisting is at $89.5^\circ$ instead of at $90^\circ$. If we were to rank the three HOMOs shown in
terms of their helicality on the basis of visual inspection, it is clear that the 0°-case is the least helical. However, we can not easily distinguish whether the end-group at 45° or 89.5° leads to the most helical MOs, or if the helicality is perhaps equal. The analysis of the cumulated sum of angles provides a quantitative answer to this problem. When the dihedral angle of the end-group is 0°, the cumulated sum of angles increases with a series of steps as we expect from a rectilinear MO. By increasing the dihedral angle of the end-groups, the cumulated sum of twist through the HOMO gradually becomes less staircase-like. Instead, it approaches the constant increase we associate with a helix. We see that increasing the dihedral angle of the end-group correlates systematically with a decrease in the MAD. Therefore, we can quantitatively say that an increase in the torsion angle gives an increase in helicality. This analysis also reveals that the HOMO does not achieve perfect helicality, instead, the increase in helicality saturates with a MAD \( \sim 30 \) as we approach a dihedral angle of 90°.

The analysis for the similar 1,6-Me-[5]cumulene is shown on the right in Figure 4. At the top right of Figure 4, we show the HOMO at six different dihedral angles for the [5]cumulene. At 0° and 180°, the \( \pi \)-orbitals have a rectilinear shape as the two \( \pi \)-orbital systems in the molecule are separated due to the \( D_{2h} \)-symmetry and the MO results from contributions from only one of the \( \pi \)-systems. Starting from 0°, as the dihedral angle between the end-groups increases the HOMO-LUMO gap narrows and at 90° the HOMO and LUMO become degenerate and cross.\(^{26}\) With increasing dihedral angle, we again see an increase in the helicality of the HOMO that saturates close to 90° and then decreases again with a further increase towards 180°. There is a notable difference from the diphenyl-diyne. The helicality increases quickly with twist, reaching a MAD \( < 10 \) already at a 20° dihedral angle then slowly decreases to a minimum MAD of 4. Thus the HOMO becomes an almost perfect helix much like the odd-carbon cumulene.

The MAD thus allows for a direct comparison of the helicality of different molecules. Comparing the \( \sim 90° \)-cases for both molecules, it is clear that the HOMOs of the [9]- and [8]cumulenes are closer to a cylindrical helix than that of the diphenyl-diyne. This underlines
that MO helicality is not just a property of the torsion angle, but depends on the chemistry of the end-groups that ultimately controls if a linear carbon chain is cumulenic or polyynic.\textsuperscript{47} This lack of perfect helicality may be linked to the more significant bond-length alternation in the diyne. We observe the maximal twist at the single bonds as this is where the occupied frontier MOs are antibonding.

**Metallacumulenes**

![Diagram of Metallacumulene](image)

Figure 5: Cumulated sum of the twist of the HOMO plotted against length along the cumulenic axis of $\text{trans-}[\text{EtC}=(C=)\text{C}=\text{Ru}=(C=)\text{CMe}]^{2+}$. The chemical structure is shown in the upper right and its HOMO is shown in the lower left of the plot. The filled circles indicate the position of atoms along the cumulenic carbon chain (black: carbon, turquoise: ruthenium) and the black, dashed line is a guide to the eye.

Metallacumulenes and -ynes are another class of molecules that may exhibit helical MOs in the linear fragments of the molecules.\textsuperscript{15,48–50} Synthesis of long $[n]$cumulenes pose a practical challenge because they are rather unstable.\textsuperscript{51} However, by complexing the cumulenes with a transition metal, the reactivity of the cumulenylidene ligands can be brought down due to both electronic and steric effects.\textsuperscript{52–56} Since the first organometallic compounds with cumulene moieties were reported by Fischer et al.\textsuperscript{57} and Berke\textsuperscript{58}, the synthesis of complexes with great structural variation continues to be an active field.\textsuperscript{59–64} Formally, the metallacumulene shown in Figure 5 has $C_1$-symmetry, and any MO-helicality will therefore not be symmetry-protected. Note that the metallacumulene illustrated in Figure 3 has had the phenyl groups...
replaced with hydrogens to speed up calculations. From the HOMO illustrated in the bottom of Figure 5, it is clear that this MO is somewhat helical. Still, visual assessment of the helicality of this MO compared with the previous MOs is challenging. Again, we plot the cumulated sum of angles through the entire molecule (blue curve in Figure 5). This helical MO deviates from a cylindrical helix as it exhibits the rounded step-like lineshape that we saw previously. We can also see that at the ruthenium center there is a jump in the evolution of the helical MO of approximately $\pi$ radians. This jump is due to the inherent sign-change in the metal $d$-orbitals that couple to the carbon $p$-orbitals. As we also saw in the previous example, the cumulated sum along the chain provides us with a richer understanding of how the helicality changes compared with visual inspection of the MO.

Due to the jump of $\pi$ radians in the cumulated sum at the ruthenium, there are two different ways of summarizing how much the HOMO deviates from a cylindrical helix. It is possible to make a straight line-fit to all the data points or, alternatively, to split the points into two sets, comprising points before or after the ruthenium where there is an inherent deviation from perfect helicality. The resulting MAD for these approaches is shown in Table 1.

| MAD               |        |
|-------------------|--------|
| Total$^a$         | 40     |
| Before Ru$^b$     | 22     |
| After Ru$^b$      | 18     |
| Mean$^c$          | 20     |

$^a$ Fit of the whole dataset.
$^b$ Fit of only the data before or after Ru.
$^c$ Mean of the MAD before and after Ru.

Comparing the two measures for the total helicality (entries "Total" and "Mean" in
Table 1), we see that, independent of which approach we choose, both suggest that the HOMO of the metallacumulene shown in Figure 5 deviates more from a cylindrical helix than the HOMO of S-1,9-Me-[8]cumulene; still, in the individual cumulenic parts the deviation is less than that in the polyynes. Comparing the MAD for the fit of the data before and after the ruthenium center ("Before Ru" and "After Ru" entries in Table 1), we see that both parts have similar MAD suggesting that the helicality of both sides of the metallacumulene are comparable. This might not be the case for other types of metallacumulenes with a different choice of substituents. The possibility of variable helicality in different parts of a single molecule means that metallacumulenes may make it possible to test how different molecular properties correlate with helicality in separate molecular components (here the ligands). It provides an interesting testbed as many other molecular properties would be kept constant, isolating the impact of helical MOs.

**Spiroconjugated molecules**

Next, we examine the simple spiroconjugated molecules 1,6-dimethylspiro[4.4]nonatetraene and 1,4-dimethylspiro[2.2]pentadiene. As with the even \([n]\) cumulenes, metallacumulenes and polyynes, the two orthogonal \(\pi\)-systems may interact and mix. However, only half of the frontier MOs of spiroconjugated molecules become helical when the molecules are appropriately substituted. As the helicality of their MOs might influence optical properties, the quantification of helicality is of interest. The carbon chain is defined as the carbon atoms in the shortest through-bond path between the methyl groups. Note that the distance between the solid circles in Figure 6 (symbolizing carbon atoms) is the bond distance between two adjacent carbons and not the z-coordinate for each carbon.

Starting with the HOMO−2 and HOMO−3 of dimethyl-spiro[4.4]nonatetraene (blue and red in the top of Figure 6), we see non-uniform helicality across the molecule. There is a linear increase/decrease evident in the cumulated sum across the center of the molecule, indicating helical orbitals, versus step-like behavior close to the methyl groups. This is hard
Figure 6: Cumulated sum of the twist of the MO twist plotted against length along the molecular axis of dimethyl-spiro[4.4]nonatetraene (top) and dimethyl-spiro[2.2]pentadiene (bottom) for selected pairs of orbitals shown in blue and red. The molecular axis is defined as the shortest through-bond path between the two methyl groups. Chemical structures of the two molecules are shown to the right in the top graph and to the left in the bottom graph. The highest occupied MO-pairs helical MO-pairs of each molecule are shown opposite to the chemical structures. The black, filled circles indicate the position of the carbon atoms along the designated carbon chain and the black, dashed line is a guide to the eye. Isovalue: 0.01 a.u.

to see by visual inspection of the MOs in the top left corner of Figure 6. Furthest away from the spiro-carbon the orbitals are more similar to the rectilinear MOs we see in the unsubstituted spiro[4.4]nonatetraene or, simply, cyclopentadiene (see Figure S3). This is also reflected in the MAD shown in Table 2: Using the full dataset gives a MAD of 17 for both HOMO–2 and 18 for HOMO–3. On the other hand, if the data set is limited to the carbons directly adjacent to the spiro-carbon, we get a MAD of 3 for the HOMO–2 and 8 for the HOMO–3. These two MAD also suggest that there is a quantifiable difference in helicality between the HOMO–2 and HOMO–3. This difference is again not clear from the isosurface plotted at the top of Figure 6, but is noticeable in the graph of the cumulated
sum. For spiro-[2.2]pentadiene (bottom of Figure 6), the angular twist of the HOMO and
HOMO-1 increases/decreases almost linearly. This is apparent both from the cumulated sum
and the MAD (see Table 2), which is very close to 1. For both molecules, their MOs hardly
deviate from a cylindrical helix when close to the spiro-carbons and, consequently, both sets
of MOs are similar to each other in this region. Moving away from the spiro-carbon, the
dimethyl-spiro[4.4]nonatetraene starts to resemble a rectilinear \( \pi \)-MO whereas the helical
character persists in the HOMO and HOMO–1 of dimethyl-spiro[2.2]pentadiene.

Table 2: MAD for line-fits to the data shown in Figure 6.

|                     | MAD  |
|---------------------|------|
| Dimethyl-spiro[4.4]nonatetraene (5 carbons)\(^a\) |      |
| HOMO – 2            | 17   |
| HOMO – 3            | 18   |
| Dimethyl-spiro[4.4]nonatetraene (3 carbons)\(^a\) |      |
| HOMO – 2            | 3    |
| HOMO – 3            | 8    |
| Dimethyl-spiro[2.2]pentadiene |      |
| HOMO                | 2    |
| HOMO – 1            | 7    |

\(^a\) Refers to length of the carbon chain across the spiro-carbon included in the fit.

Cycloallenes

Finally, we examine cyclic allenes where the allenic moiety is constrained, thus perturbing
the helical \( \pi \)-system. Cycloallenes are synthetically interesting compounds that, given their
reduced symmetry due to the ring structure, exhibit helical MOs.\(^{29,30,71–75}\) Most recently,
Ramirez et al.\(^{30}\) demonstrated that secondary orbital interactions due to the helical frontier
MO topology are responsible for the \textit{endo} selectivity in Diels-Alder reactions. Four molecular
structures of simple cycloallenes are shown in the top of Figure 7, from left to right, 1,2-
cyclohexadiene, 1,2-cycloheptadiene, 1,2-cyclooctadiene and 1,2-cyclononadiene. Unlike the
linear carbon chain in allene, cycloallenes are strained compounds where the two cumulated
double bonds sit at a slightly bent angle relative to each other. This angle approaches 180° with increasing ring size, and will thus eventually be close to 1,3-dimethylallene.\textsuperscript{76}

The HOMO for each of the four cycloallenes is shown in Figure 7. While it is visually clear that these four MOs are helical, it is not clear how their helicality rank relative to each other. Looking at the cumulated sum of twist along the carbon chain, we can see that the helicality of all four MOs is similar and follows the same trend. All four have an almost linear increase of the cumulated sum with a slight flattening close to the allenic carbon. This also means that all four have a high degree of helicality with a MAD below 3.5 as seen in the bottom plot of Figure 7. Comparing the helicality of the four cycloallenes with 1,3-diMe-allene, we see that the helicality of the cycloallenes approaches the helicality of the 1,3-diMe-allene with increasing ring size as expected. The bending of the cumulated double bonds introduced by the ring has only a minimal effect on the helicality. The introduction of cyclic substituents further enables the fine-tuning of the helical MOs without destroying helicality.

Conclusions

In this work, we have developed a method that can determine how the helical twist of \( \pi \)-MOs evolve through any given molecule. This method can be used to quantify the deviation of the MO from a perfect cylindrical helix and thus allows us to probe the helicality of MOs for a diverse set of molecules. We find a pronounced difference in the change in helical curvature of the \( \pi \)-MOs of different types of linear systems. Notably, the MOs of polyynes do not achieve the same level of helicality as equivalent-length cumulenes. The distribution of helical twist of the MOs depends on the chemical nature of the \( \pi \)-system. This change in uniformity of the twist is not tied to the difference between polyynic and cumulenic systems as the staircase-like features, and this change in helicality, are also present in the investigated metallacumulene, \( \text{trans-}[\text{EtC=}(\text{C=})_4\text{C=Ru=(C=})_4\text{CMe}]^{2+} \). The degree of helicality is very
sensitive to some types of structural changes while being almost invariant to other types. For example, twisting the end-groups of polyynes and cumulenes has a considerable effect on the helicality of their MOs. Contrarily, the bent bond angles in cycloallenes has negligible effect on the helicality of their HOMO. Our method allows for a straightforward and systematic analysis of a range of molecular systems independent of how each system is partitioned.

Going forward, the development of tools for systematical quantification of helicality in MOs is a prerequisite to investigate how helical MOs correlate with, or can be used to predict, molecular properties. This might, for example, allow us to control molecular properties based on our knowledge of how to chemically manipulate helical MOs. As we become increasingly aware of molecules where helical $\pi$-systems appear, the need grows for better tools to make quantitative assessments of helicality. In this work we have used MAD as the quantitative descriptor of orbital helicality, because it both summarizes how well the data follows a given model and allows for comparison across data sets. While there may be
more elaborate measures that could be envisaged, it is a simple, intuitive, and well-known assessment approach. The use of MAD as the test for cylindrical helicality answers the following question: Is the MO a perfect helix or not? While the case of a cylindrical helix is well-defined and corresponds to a MAD of 1, the "or not"-situation is less well-defined as there will be more situations that deviate a cylindrical helix. In practice, this is not a problem in the present study. However, future work may aim for a more distinct definition of the edge-cases, especially if MO helicality turns out to be decisive for molecular properties.

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