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The fundamental relation between electrohelicity and molecular optical activity

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Electrohelicity arises in molecules such as allene and spiropentadiene when their symmetry is reduced and helical frontier molecular orbitals (MOs) appear. Such molecules are optically active and electrohelicity has been suggested as a possible design principle for increasing the chiroptical response. Here we examine the fundamental link between electrohelicity and optical activity by studying the origin of the electric and magnetic transition dipole moments of the $\pi - \pi^*$ transitions. We show that the helical character of the MOs drives the optical activity in allene, and we use this knowledge to design allenic molecules with increased chiroptical response. We further examine longer carbyne-like molecules. While the MO helicity also contributes to the optical activity in non-planar butatriene, the simplest cumulene, we show there is no relation between the chiroptical response and the helical π -MOs of tolane, a simple polyyne. Finally, we demonstrate that the optical activity of spiropentadiene is inherently linked to mixing of its two π -systems rather than the helical shape of its occupied π -MOs. We thus find that the fundamental connection between electrohelicity and optical activity is very molecule dependent. Although electrohelicity is not the underlying principle, we show that the chiroptical response can be enhanced through insight into the helical nature of electronic transitions.

1 Introduction

The chiroptical properties of a molecule are fundamentally linked to the interaction between the electromagnetic wave of circularly polarized light and charge in the molecule during its electronic transitions. While the electric transition dipole moment, $\vec{\mu}$, arises from linear charge displacement, the magnetic transition dipole moment, \vec{m} , arises from rotation of charge.^{1,2} Equivalent to the way we envision circularly polarized light as an electric field vector that propagates helically in space, charge needs to be helically displaced in the molecule for the transition to be optically active. Helical topology in the frontier π -orbitals has been suggested as an avenue for designing optically active molecules.³⁻⁶ This orbital effect has been coined electrohelicity.⁷ However, its experimental relevance is limited by the simultaneous presence of both helicities in the electronic structure.⁸ Nonetheless, relations to single-molecule conductance, 9,10 reaction selectivity, 11 and optical properties 12-15 have recently been suggested. Is the electrohelicity effect a fundamental cause for a strong chiroptical response?

Electrohelicity appears as helical molecular orbitals (MOs) in allene and spiropentadiene when their symmetry is reduced from D_{2d} to D_2 (or C_2).^{7,15–19} In allene both the degenerate sets of highest occupied MOs (HOMOs) and the lowest unoccupied MOs (LUMOs) are helical (Figure 1 left). In spiropentadiene



Fig. 1 Frontier MOs of allene and spiropentadiene computed at the reduced D_2 symmetry with irreducible representations provided in both D_{2d} and D_2 point groups. Computed at the wB97X-D/def2-TZVP level.

only the HOMOs are helical while the non-degenerate LUMO and LUMO+1 are delocalized due to spiroconjugation (Figure 1 right).^{20–24} These helical frontier MOs are present in several types of linear carbyne-like and spiroconjugated molecules due to the Möbius topology of the π -system.^{7,19,25–30}

We recently demonstrated a correlation exists between the chiroptical response and the splitting of the near-degenerate helical MO pairs in substituted allenes and longer odd-carbon cumulenes.⁶ In this article, we examine the underlying connection between electrohelicity and optical activity in molecules where helical frontier MOs appear. We treat four types of molecules that

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Fig. 2 Schematic and DFT-computed HOMO, LUMO, transition density and transition dipole moments of the $S_0 \rightarrow S_1$ electronic transitions of ethene (a) and formaldehyde (b). Charge depletion is shown in white (\ominus in schematic), charge increase in light-blue(\oplus in schematic).

exhibit electrohelicity: Subsection 3.1 covers allene, 3.2 evencarbon cumulenes, 3.3 polyynes, and 3.4 spiropentadiene. Each of these subsections can in principle be read independently of each other. First, we show that the optical activity of chiral allenes is driven by the helicity of the frontier MOs, and we demonstrate strategies for optimizing the chiroptical response. Then we examine linear and spiroconjugated systems where the helical frontier MOs may not contribute directly to the optical activity. Finally, we discuss the potential implications of these results going forward in the conclusions section.

2 Theory

Optical activity of electronic transitions in the UV-Vis range is measured by electronic circular dichroism (ECD) as the difference in absorption of left and right circularly-polarized light, $\Delta \varepsilon$. Whereas the absorption is theoretically connected to the oscillator strength of the transition, the chiroptical response is proportional to the rotatory strength of the transition, $\Delta \varepsilon \propto R$. In its simplest form, *R* is given by the product of the lengths of the electric ($\vec{\mu}$) and magnetic (\vec{m}) transition dipole moment vectors and the angle given by their mutual orientation (θ) as given in equation 1.

$$R = |\vec{\mu}| \cdot |\vec{m}| \cdot \cos(\theta) \tag{1}$$

It follows from this equation that both $\vec{\mu}$ and \vec{m} must be non-zero and oriented non-perpendicularly for a transition to be optically active. Often transitions with high *R* are electrically allowed and therefore driven by large $\vec{\mu}$, which, while enhancing $\Delta \varepsilon$, reduces the dissymmetry factor, $g = \Delta \varepsilon / \varepsilon$, at a given wavelength. Ideally, optically active transitions must be both magnetically and electrically allowed to facilitate both high absolute and relative optical activity as given by $\Delta \varepsilon$ and g.^{1,2,31,32}

Electrically allowed transitions have a linear displacement of charge that give rise to $\vec{\mu}$. For a simple electronic transition, e.g., HOMO \rightarrow LUMO, the transition density is calculated from the direct product of the implicated MOs of the transition, which gives rise to the transition dipole moments. In the $\pi \rightarrow \pi^*$ transition of ethene shown in Figure 2a, there is a phase-difference in one end of the molecule. Consequently, charge is depleted in one end and increased in the other end, leading to $\vec{\mu}$ pointing along the molecular axis, and the $S_0 \rightarrow S_1$ transition of ethene is electric

dipole allowed. Without rotation of charge, \vec{m} is zero.^{1,2}

An example of a magnetic-dipole allowed transition is the HOMO \rightarrow LUMO ($n \rightarrow \pi^*$) transition of formaldehyde shown in Figure 2b. The nodal planes of the HOMO and LUMO have different orientation and the product therefore gives a quadrupole. When the electric quadropole is associated to a rotation of charge it gives rise to the magnetic transition dipole moment. The direction of \vec{m} depends on the direction of the rotation as given by the *right-hand rule*. The net direction of rotation around the molecular axis is not defined for an achiral species such as formaldehyde, and the direction of \vec{m} in Figure 2b is arbitrarily chosen. This analysis enables us to pinpoint that the $S_0 \rightarrow S_1$ transition is optically inactive because it is electric-dipole forbidden.^{1,2}

The chiroptical response of a molecule thus depends on the chirality contained in the electronic structure, not specifically the chiral arrangement of atoms in the molecule. There is no direct correspondence between an enantiomer's chiral configuration and the chiroptical sign of its electronic transitions. From the basics of MO theory it is evident that there must be both linear and rotational displacement of charge during a transition if it is to be both electric- and magnetic-dipole allowed. Furthermore, the angle of the dipoles must be as close to (anti-)parallel as possible to optimize the chiroptical response (see equation 1). To achieve this, the transition density must have a helical shape. This is the fundamental theoretical concept that governs electronic circular dichroism and circularly polarized luminescence spectroscopy.^{32–36}

The optical properties of molecules are computed using response theory as implemented in time-dependent density functional theory (TD-DFT) in the Gaussian16 code.^{37,38} The rotatory strengths, electric and magnetic transition dipoles associated to each electronic transition are computed directly this way, and we report them in cgs-units to provide scale of the magnitude of the dipole vectors; see SI part 1 for a note on unit conversion. Geometry optimization and single-point computations were carried out using DFT with the ω B97X-D functional and the def2-TZVP basis set as implemented in Gaussian16.^{38–40} Molecules were optimized to the *tight* criterion using the *ultrafine* grid setting. To construct torsion profiles, the dihedral angle between end-groups of allene and spiropentadiene structures is changed without further optimization. MOs are plotted with an isosurface value of



Fig. 3 Direct products of the π -MOs, electric (blue) and magnetic (red) transition dipole moments, and rotatory strengths for the direct MO products and for the electronic transitions (right column) of allene treated in D_2 symmetry. $\vec{\mu}$ is in 10^{-18} esu·cm. \vec{m} is in 10^{-21} erg/G. R is in 10^{-40} erg·esu·cm/G.

0.02 and transition density isosurfaces with a value of 0.0005.

3 Results

Our goal is to gain insight by assessing the π -MOs and the optical activity of the related $\pi - \pi^*$ transitions. We initially treat the achiral (D_{2d}) allene in quasi- D_2 symmetry in Subsection 3.1. This exercise lets us examine the underlying relation between optical activity and helical MOs without substituents. Furthermore, we gain insight into the limit where allene changes from optically inactive to active when mirror symmetry breaks (cf. ESI Figure S1 when rotation symmetry breaks).

We proceed by applying this understanding of allene to explore the potential for achieving high optical activity in functionalized systems. Next, in Subsections 3.2 and 3.3 we treat an even-carbon cumulene and a polyyne subjugated to torsion, which have helical MOs similar to those of allene, and we discuss whether the helicity contributes to the chiroptical response. Finally, we treat achiral (D_{2d}) spiropentadiene in quasi- D_2 symmetry to assess how the optical activity differs in spiroconjugated systems, which are structurally different from the carbyne-like allenes.

3.1 Allene

We start by assessing the parent allene molecule in quasi- D_2 symmetry where only the three rotation axes are preserved. In D_2 symmetry the HOMOs and LUMOs are helical and the four transition densities arising from the direct MO excitations are shown in Figure 3. Products of MOs of the same helicity give a helical transition density that retains the helicity (*P* or *M*). Accordingly, these have notable electric and magnetic transition dipole moments. $\vec{\mu}$ is aligned along the z-axis of the molecule (the allenic axis). \vec{m} has a non-zero component along the z-axis and a larger compo

nent pointing in-between the two allenic planes, which results in an 80° angle between the two transition dipole vectors. As illustrated in Figure 3, the direction of \vec{m} is in accordance with the right-hand rule considering the helicity of the transition density. The big off-axis component of \vec{m} comes from the linear charge displacement that is characteristic for $\pi - \pi^*$ transitions; thus the helix pitch is big and the charge does not rotate perfectly around the allenic axis. Only the z-component (\vec{m}_z) aligns with $\vec{\mu}$ (equation 1), which is pointing along the allenic axis.⁴¹ To provide a sense of an upper-bound for the rotatory strength of substituted allenes, we can calculate *R* for this transition density that is associated to the MO transitions. The z-component of \vec{m} is parallel to $\vec{\mu}$ for $\pi_P \rightarrow \pi_P^*$ giving positive *R* and anti-parallel for $\pi_M \rightarrow \pi_M^*$ giving negative *R* of $\pm 156 \cdot 10^{-40}$ erg·esu·cm/G.

The helical MO transitions belong to the b₁ irreducible representation and mix by linear combinations into non-degenerate transitions.^{42–44} The resulting transition dipoles into the two B₁ excited states are shown in the right column of Figure 3; either $\vec{\mu}$ or \vec{m}_{τ} cancels out, and the two transitions are optically inactive. The transitions involving MOs of differing helicity also mix in similar fashion (bottom rows of Figure 3); those two are totalsymmetric and are electric and magnetic dipole forbidden. We thus see why the allene transitions are optically inactive. It is the linear combination of the two helical MO transitions ($P \pm M$, Figure 3) that limits the optical activity of allenic molecules. The D_{2d} -structure represents a case where the orbital helicity is perfectly cancelled. To increase the optical activity we must split the degenerate helical MOs, so they will not contribute equally to the excited states. This is the principle of electrohelicity-driven optical activity in allene, and we will explore how this is applied in terms of molecular design.

3.1.1 Torsion of Allenes

Axial torsion of allene reduces its symmetry to D_2 and splits the helical MO pairs as the helix either unwinds and become more bonding (lower eigenvalue), or overwinds and becomes more antibonding (higher eigenvalue).^{7,10,15,19,25–28} Consequently, the two helical components of the transition do not contribute equally when the dihedral angle is changed from 90°, and the transitions become optically active. This is demonstrated in Figure 4, where the end-group orientation of allene is changed, and the energies of the two B_1 excited states change accordingly. As the opposing helical components are emphasized in each transition, the rotatory strength increases systematically with differing sign for both transitions. The 2B₁ state becomes more active as it is the one that is electric dipole allowed at 90°.



Fig. 4 Torsion of allene in its reduced D_2 symmetry. a) Diagram of $\pi \to \pi^*$ electronic transitions of allene during axial torsion. b) Rotatory strength as function of torsion angle in allene and cycloallene series. Note that the 2A and 3A states of allene are omitted for clarity as they are optically inactive independent of the torsion angle.

Torsion of allene is realized in a series of cyclically alkylsubstituted allenes, where the alkyl linker constrains the structure. These have been synthesized and studied for their helical MOs in other contexts. ^{11,15,30,45} The series of cycloallenes have a perturbed structure where both the allenic bond angle and dihedral angle are distorted. The frontier MOs and electronic transitions of allene are retained in the cycloallenes at the same torsion angle (ESI Figure S2). As the helical MOs are split energetically they do not contribute equally to the electronic transitions, and consequently the cycloallenes have improved chiroptical response at more acute torsion angles (Fig. 4b). This exemplifies how the energetic tuning of the helical frontier MOs of allene can be used to optimize its optical activity.

3.1.2 Substituted Allenes

Saturated substituents that hyperconjugate into the helical π -system break the degeneracies of the frontier π -MOs.^{6,9,46} Breaking the symmetry of allene with simple substituents such as in 1,3-dimethylallene makes the molecule optically active. However, the rotatory strength of the allowed $S_0 \rightarrow S_4$ transition is still modest (Table 1) because the helical frontier MOs remain

near-degenerate. If ethyl substituents are used instead, the rotatory strength comes close to the limit of the pure MO transitions $(156 \cdot 10^{-40} \text{ erg.esu.cm/G}, \text{Figure 3})$. While the substituents themselves may also contribute to increasing the rotatory strength, this enhancement is primarily driven by the perturbation of the allene π -system. As a control, we can place one or two ethyl substituents at the 1-position instead of at the 1,3-positions (ESI Figure S3). Despite all molecules having similar low symmetry (Table 1), the increase in the rotatory strength is much smaller because the substituent pattern in ethylallene and 1,1-diethylallene does not fully retain the helical frontier MOs and break their degeneracy. This is also evident for 1,3-diethylallene as its optical activity will depend on the conformation of the substituents.^{6,47} We described this mechanism in detail in a previous communication.⁶

Table 1 Rotatory strength of $\mathsf{S}_0\to\mathsf{S}_4$ transition of substituted allenes

Molecule	Point Group	R (10^{-40} erg·esu·cm/G)
	D_{2d}	0
	<i>C</i> ₂	55
	C_2	141
	<i>C</i> ₁	35
	C_2	82

3.1.3 Bis-allenes

Another avenue for enhancement of the optical activity of lowsymmetry allenes is through its covalent dimers, bis-allenes. A number of such molecules have been synthesized with different orientations of the allenic units. $^{48-53}$ The frontier MOs of the allene units mix into combinations of the helical MOs, which are thus partially retained (ESI Figure S4). The electronic transitions are composed similarly to those of allene. We examine an allene dimer where the allenic units are placed in parallel and rotated relative to each other, and two bis-allenes where the allene moeities have similar orientation (Figure 5a). The allene dimer is shown at 45°. The hypothetical Bis-allene1 has an angle of 45°, while silicon-based Bis-allene2 at 56.7° was synthesized by Lin et al. ⁵¹ All three have D_2 symmetry and we look at the 2B₃ excited state where the large off-axis component in \vec{m} of allene (cf. Figure 3) enables high optical activity.

The two MO excitations that contribute to the $2B_3$ transition of the 45° allene dimer are shown in Figure 5b. The MOs are in-phase (HOMO-1 and LUMO) and out-of-phase combinations (HOMO and LUMO+1) of helical MOs. As in the optically active transitions of allene, the MO helicites match for the occupied and unoccupied MOs. The direct MO products thus look like those of allene with a clear helical movement of charge in each allenic unit. As the allenic units are rotated 45° relative to each other, the electric and magnetic dipole moment point out of the screen, towards the viewer. The same transition is shown for Bis-allene1 in Figure 5c. Again, it is visually clear that the helical components of the transition contribute significantly to the optical activity of



Fig. 5 a) allene dimer, alkyl-linked bis-allene1, and silyl-linked bis-allene2 (TMS: trimethylsilyl). Angle between the allenic units is given. b-c) Direct product of the frontier MOs that contribute to the transition into the 2B₃ excited state of the 45° allene dimer (b) and bis-allene1 (c). d) Rotatory strength as function of the angle between the allenic units of the allene dimer, and the two bis-allenes. MO iso-value = 0.04 and Charge iso-value = 0.001 are used for clarity.

the transition. The dihedral angle dependence of the rotatory strength of the dimer and the two bis-allenes is plotted in Figure 5d. The rotatory strength of the allene dimer maxes at $642 \cdot 10^{-40}$ erg·esu·cm/G at 56° orientation of the dimer. The two bis-allenes do not reach this level, but nonetheless the optical activity is significantly improved from monomer allene. The design of optically active allene-based macromolecules may benefit from considering the helical electronic structure of allene. We aim to explore such design rules in a future study.

3.2 Even-carbon Cumulenes

Allene is the shortest of the series of odd-carbon cumulenes. The even-carbon series of cumulenes are much more explored due to their increased synthetic availability relative to the odd-carbon series.^{54–57}They have co-planar end-groups in the ground-state structure,⁸ and achieves helical frontier MOs as its symmetry is reduced by torsion of the end-groups.



Fig. 6 Direct product of the frontier MOs that contribute to the transitions into the $1B_1$ and $2B_1$ excited states of butatriene at 0° (a) and 10° (b) torsion. c) Rotatory strength as function of the dihedral angle between the end-groups of butatriene.

As the end-groups of butatriene ([3]cumulene) are rotated out of plane, its two π -systems mix and even at small dihedral angles the MOs achieve visually clear helical character. ^{10,19,26,30} Shown in Figure 6a, the first two excited states belong to the B_1 irreducible representations and each have clear HOMO->LUMO and HOMO-1 \rightarrow LUMO character. At 0°, the HOMO \rightarrow LUMO transition is electric dipole allowed, while the HOMO-1→LUMO is magnetic dipole allowed. Already at 10° torsion, the HOMO and HOMO-1 have become very helical, while the LUMO only has weak helical character that becomes visually clear at higher dihedral angles (Figure 6b). The transition density also achieves helical character. Especially in the case of the HOMO-1 \rightarrow LUMO transition where the MO have same helicity, it is visually clear that the helicity of the MOs lead to a helical rotation of the charge. Both transitions achieve parallel non-zero $\vec{\mu}$ and \vec{m} . The dihedral angle dependence of the rotatory strength (Figure 6c) reveals that both transitions quickly achieve an enhanced chiroptical response as the MOs become helical. We note that the two electronic transitions cross at 17° torsion in an avoided crossing, and thus both MO transitions contribute significantly to both electronic transitions in the vicinity of this dihedral angle. Although the mixed contributions from several MO excitations may factor in, it is visually clear that the MO helicity makes a significant contribution to the optical activity of non-planar butatriene.

3.3 Polyynes

Polyynes are structurally similar to even-carbon cumulenes but are more stable due to the single-triple bond topology, and is thus an oft-used motif for molecular linkers.⁵⁸⁻⁶¹ As in cumulenes, when the end-groups are rotated polyynes become optically active. Some π -orbitals become helical as the symmetry is reduced and the π -systems mix. The mixing is much less significant than in the cumulenes, and at small torsion angles the mixing is not visually clear (Figure 7a). Although the HOMO and LUMO only achieve weak helicity, there are lower-lying π -MOs that become more helical. 5,7,25,28,30 The HOMO-LUMO transition of tolane is electric-dipole allowed and becomes optically active with torsion. Just as there is no visually clear helicity in the MOs, there is no significant helicity in the transition density (Figure 7a). While there is charge rotating around the polyynic wire in both transitions at high torsion angles, it seems that it is primarily the components on the terminal phenyl groups that gives a non-zero \vec{m} . This charge rotation between the phenyl groups increases with higher torsion angle. The rotatory strengths therefore increase until the phenyl groups are almost in perpendicular orientation, as plotted in Figure 7b.

At high dihedral angles, close to perpendicular orientation, the B_1 transitions are dominated by the HOMO \rightarrow LUMO and the HOMO $-1\rightarrow$ LUMO+1 excitations with 79% contribution each to the electronic transitions at 80° torsion. Though the MOs are helical at near-perpendicular torsion angles, helicity is insignificant in the transition density because the helical components of the MOs are opposite. Through the full range of dihedral angles it is the twisted orientation of the end-groups that is responsible for the magnetic transition dipole. We find that this is also the case for higher-lying excited states of tolane that are optically active; it seems they are all driven by the charge moving between the two terminal phenyl groups and therefore those transitions are thus not of particular interest for this study. The helical MOs of tolane do not contribute to its optical activity. It is yet to be said, if this result is general for all polyynic molecules or specific to tolane.

3.4 Spiropentadiene

Spiropentadiene has D_{2d} symmetry, and like allene we assess it in quasi- D_2 symmetry. When the symmetry is reduced, the π systems mix and the occupied π -MOs become helical (Figure 1) with a continuous π -nodal plane spanning the entire length of the molecule. As we have discussed in detail in recent work, ¹⁵ the (near-)degenerate sets $\pi \to \pi^*$ transitions are separated by symmetry, and the two HOMO \rightarrow LUMO transitions shown in Figure 8 do not mix. The HOMOs differ in helicity, while the LUMO is a non-helical spiroconjugation MO. Their products show weak linear and circular charge displacement and consequently both $\vec{\mu}$ and \vec{m} are relatively small in magnitude, and it is hard to visually identify any helical components in the transition density. $\vec{\mu}$



Fig. 7 a) Direct product of the frontier MOs that contribute to the transition into low-lying B₁ excited states of tolane at 10°, 45°, and 80°. (b) Rotatory strength as function of the dihedral angle between the phenyl groups of tolane.

and \vec{m} both point between the two molecular planes. The two transitions are energetically degenerate and the opposite signs of *R* thus cancel out in an ECD spectrum; consequently the unsubstituted molecule is optically inactive. The same is true for the HOMO \rightarrow LUMO+1 transitions (ESI Figure S5).

The chiroptical response is enabled by the parallel orientation of the transition dipoles (Figure 8). It is the mixing of the π systems through the formally saturated central spiro-carbon that ensures the electric and magnetic transitions dipole moments are reoriented. If we remove rotation symmetry and treat spiropentadiene as quasi- $C_{2\nu}$, the transition density of the electronic transitions is contained within one of the molecular planes (ESI Figure S6). Consequently, spiropentadiene is optically inactive because $\vec{\mu}$ and \vec{m} are perpendicularly oriented.

The mixing of the two π -systems in quasi- D_2 symmetry mediates the optical activity. However, it appears that the rotatory strengths are not mediated by the MO-helicity as such. This is also evident by $\vec{\mu}$ and \vec{m} not pointing along the helical axis of the MOs, as they do for the allene and butatriene. Delocalization of the π -systems has been demonstrated to affect the optical properties of spiropentadienes, ⁶² and this is also the case for the chiroptical response here. Although the optical activity is not driven by electrohelicity, we showed in a previous communication that the helicity manifests in the electron density, ¹⁵ which changes in



Fig. 8 Direct products of the two HOMO \rightarrow LUMO transitions of spiropentadiene in D_2 symmetry viewed from end and side of the molecule. The electric (blue) and magnetic (red) transition dipole moments, and the rotatory strengths is provided for the electronic transitions (right column). $\vec{\mu}$ is given in 10^{-18} esu·cm. \vec{m} is given in 10^{-21} erg/G. R is given in 10^{-40} erg·esu·cm/G.



Fig. 9 Torsion of spiropentadiene in its reduced D_2 symmetry. a) Diagram of $pi \rightarrow \pi^*$ electronic transitions of spiropentadiene during axial torsion. b) Rotatory strength as function of torsion angle of spiropentadiene and cyclospiropentadiene series (cyclo-spde).

a helical fashion when charge is transferred from helical to nonhelical MOs during the four $\pi - \pi^*$ transitions.

Splitting the (near-)degenerate transitions may enhance the ECD response because transitions with opposite rotatory strengths move towards different wavelengths. As as showed for allene, this can be achieved by axial torsion of the molecule, which in particular affects the eigenvalues of the helical MOs. However, as plotted in Figure 9, torsion also affects the rotatory strengths, which weaken with torsion for many of the transitions. Figure 9b also includes an assessment of a series of hypothetical conformationally-locked cyclic spiropentadienes. Their torsion angles are constrained by the alkyl linkers, and their electronic transitions show reasonable correlation with the constrained nonlinked systems for most of the transitions (ESI Figure S7). With the reduction of the rotatory strength, it seems that splitting the near-degenerate electronic transitions has limited potential for enhancing the chiroptical response of spiropentadiene derivates.

4 Conclusions

We have assessed the relation between electrohelicity and optical activity by analyzing the MO contributions to the electric and magnetic transition dipole moments. In allene and longer cumulenes there is a fundamental connection between their chiroptical response and helical frontier MOs, which we use for rational design of optically active molecules. However, we also show that the link is not universal, as we find no direct relation between orbital helicity and optical activity in polyynes and spiroconjugated molecules. There is thus a notable variation in the origin of enhanced rotatory strengths in molecules with electrohelicity.

These results question if electrohelicity is at all useful as a general concept for understanding and developing novel optically active molecules. When helical π -systems are suggested as an underlying mechanism for a large chiroptical response, it must be supported by careful analysis on a case-by-case basis. Indeed, we found that in allenic systems, such a mechanism involving helical MOs can be used to enable enhancement of optical activity using substituents and macrostructures. This insight is to be applied for design of molecules with large chiroptical response.

Conflicts of interest

There are no conflicts to declare.

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