The two π-systems of allene can mix into helical molecular orbitals (MOs), yet the helicity is lost in the π-π* transitions. In spiroconjugated molecules the relative orientation of the two π- systems is different as only half the π-MOs become helical. Consequently, the helicity of the electronic transitions is symmetry protected and thus helical π-conjugation can manifest in observable electronic and chiroptical properties.
The two π-systems of allene can mix into helical molecular orbitals (MOs), yet the helicity is lost in the π-π transitions. In spiropentadiene, the relative orientation of the two π-systems is different as only half the π-MOs become helical. Consequently, the helicity of the electronic transitions is symmetry protected and thus helical π-conjugation can manifest in observable electronic and chiroptical properties.

Allenes, cumulenes, and polyynes have two perpendicular π-systems, which lie in each their plane.1, 2 One may intuitively expect the π-electrons to be separately delocalized in the molecular planes. However, the two π-systems can mix, and consequently the electrons may not be restricted to the planes. In allene (Scheme 1), the orbital-mixing is mediated by the p-orbitals on its central sp-hybridized carbon as shown in Figure 1. Whenever we consider these two p-orbitals, an initial choice is made for their orientation.3, 5 By convention, we orient allene relative to its two mirror-planes. Shown in Figure 1a, the p_x and p_y basis functions will each have optimal overlap to one end of the molecule. However, the p_x and p_y basis functions can be rotated 45° around the allenic axis by making linear combinations of the two as shown in Figure 1b. This forms a so-called coarctate orbital system, which means there is continuous π-overlap between the carbon termini despite their 90° relative orientation.6 6 The choice between these two orientations is arbitrary.3, 4

More recently, Honda et al., synthesized a radical cation of spiropentasiladiene (Scheme 1) and found that spin and charge can delocalize between its two perpendicular π-systems.7 Let us consider the carbon-analogue spiropentadiene (Scheme 1). Its two π-systems are connected through a formally saturated spiro-carbon.6, 9 Shown in Figure 1b, we can make the same orbital rotation in spiropentadiene as we did for allene. The p-orbitals on the formally saturated spiro-carbon will participate in the σ-bonds of the molecule and are normally considered in the form of sp-hybrid orbitals. However, these p-orbitals are mathematically part of the carbon basis set and are available as relay orbitals for the through-bond coupling between the two π-systems. In similar fashion, σ-orbitals mediate through-bond coupling between the perpendicular π-systems in larger tricyclic analogues of spiropentadiene (Scheme 1) as described by Gleiter and co-workers.10, 11

![Figure 1. p-orbitals of the central carbon atom represented in two different rotations of allene (a) and spiropentadiene (b).](image)

In chiral allenes, cumulenes, and polyynes the electron delocalization between the two π-systems is expressed in the form of helical MOs.3, 12, 11 This helical π-conjugation is also called the electrohelicity effect. While the molecules where this effect appears are single-handed chiral, both helicities are present in the electronic structure. The chirality associated with the electronic structure is thus more complex than that of the molecular structure.14 The optical activity of odd-carbon...
cumulenes is limited by the near-degeneracy of their helical MOs. Although the helical HOMO and HOMO-1 can be split energetically by substituents, \cite{15, 16-17} it seems that the dual-helicity limits the possibility of experimentally observable effects arising from the MO helicity. Still, relations to molecular properties have been proposed. \cite{12, 18-23} Given that the through-bond electron delocalization in spiroconjugated molecules is closely related to that in allene (Figure 1), an interesting question is whether different types of π-systems are also limited by the dual-helicity of the MOs?

Here we describe the helical π-conjugation in allene and spiroconjugated molecules. We demonstrate that in the latter both the electronic structure and π→π* transitions have distinct helicity because it is symmetry protected. We revisit the π→π* transitions of allene derivates, which are the simplest species with helical MOs. Due to the symmetry of allene its electronic transitions are limited by the dual-helicity of the MOs, and we examine why spiroconjugated molecules do not suffer from this limitation. Finally, we discuss the experimental implications of optical transitions with helical change of electron density and high rotatory strengths that correlate with the helicity.

Allene is routinely described as having two orthogonal π-systems lying in each of their plane. \cite{1, 2} The highest occupied MO (HOMO) and HOMO-1 are degenerate π-orbitals as shown in Figure 2a. However, when the symmetry of the molecule is reduced from $D_{2d}$ to $C_2$ by substituting two of the hydrogens, the π-systems mix and helical π-MOs are formed. \cite{3, 12} In the case of R-1,3-dimethylallene the HOMO is an M-helix and the HOMO-1 is a P-helix. In $D_{2d}$-allene, the resulting π→π* transitions are limited between the two degenerate occupied and two degenerate unoccupied π-MOs consist of the four possible linear combinations of excitations between the two sets of MOs. The four transitions are non-degenerate and belong to $A_2$, $B_1$, $A_1$, and $B_2$ irreducible representations as outlined in Figure 2b. \cite{24} Only the $B_1→B_2$ transition is allowed (same irreducible representation as $\mu_{xz,xy}$). The substituents change little, and the first three transitions remain quasi-forbidden in dimethylallene. The effect of substituents and solvents on the optical properties of allene has been studied in great detail, and we refer to the extensive literature for analysis of their spectra. \cite{15, 25-27} The transitions of dimethylallene are almost equally-weighted combinations of excitations from occupied πMOs to unoccupied πMOs. Oscillator strengths and the specific MO weights will be method dependent, see computational details in ESI part A.

Figure 2c shows the change of electron density during the π→π* transitions of R-1,3-dimethylallene. The change of density appears primarily in the two planes of the molecule and there is this little indication of mixing between the two π-systems. We attribute this lack of helicity to the dual-helicity of the HOMO and HOMO-1. The four π→π* transitions of dimethyl allene are superpositions of helical MO excitations (see schematic overview in Figure 54 and S5). Any individual excitation involving helical MOs yields a helical pattern in the change of electron density; however, transitions between their linear combinations show a linear pattern.

In spiroconjugated molecules, two π-systems are separated by an $sp^3$-hybridized carbon atom. \cite{8} The two π-systems are oriented 90° relative to each other and interact by a well-described through-space interaction. \cite{28} Still, the π-electrons are not fully delocalized between the two rings in carbon-based spiroconjugated systems. \cite{29, 30} Spiropentadiene is the simplest case, constituting two ethene units fused together through a fifth spiro-carbon. Similar to allene, the parent spiropentadiene has $D_{2d}$ symmetry with four π-electrons. \cite{21} A fairly unstable motif due to bond strain, \cite{32} spiropentadiene has been synthesized with some variation including its sila- and germ-analagous. \cite{33, 36} Shown in the left column of Figure 3a, its HOMO and HOMO-1 are degenerate and each have clear π-character on one side of the molecule. The LUMO and LUMO+1 are non-degenerate and the two π-segments mix due to through-space π-overlap, which is characteristic of spiroconjugated systems. \cite{8, 9, 28} The dissubstitution we performed on allene has a similar effect on spiropentadiene (Figure 3a). The symmetry is reduced from $D_{2d}$ to $C_2$ and the degenerate πx and πy mix through-bond via the central carbon atom into helical πx and πy. This MO-mixing is similar to that seen in saturated triangulenes where helical σ-orbitals appear, \cite{37} but in dimethylspiropentadiene π-orbitals of both helicities are present. The unoccupied πxy* and πxy* are largely unchanged by the methyl substituents.

Figure 2. a) HOMO-1 to LUMO+1 of allene and R-1,3-dimethylallene. b) Overview of their first four electronic transitions, and their symmetry designations. Electric-dipole \((\mu_{xz,xy})\) allowed transitions are in blue. c) Change of electron density for the $S_1→S_2, S_p→S_2, S_p→S_2$, and $S_p→S_2$ transitions of R-1,3-dimethylallene. Oscillator strengths, $f$, are dimensionless. Rotatory strengths, $R$, are in $10^6$ erg-esu-cm/Gauss. Depletion of density is in orange. Computed at the B97X-D/Def2-TZVP level of theory.
The four $\pi \rightarrow \pi^*$ transitions in $D_{2d}$-spiropentadiene will be two degenerate pairs belonging to the E representation (direct products of the E with $A_2$ and $B_1$ representations in Figure 3b). All four $\pi \rightarrow \pi^*$ transitions are electric-dipole allowed (belonging to one of the irreducible representation of $\mu_{\pi,\pi^*}$), and this does not change when the symmetry is reduced by substituents. In dimethylspiropentadiene the electronic transitions become non-degenerate, but do not split by much energetically. Different from dimethylallene, the transitions are not equally weighted linear combinations. Take the two lowest energy MO excitations; $\pi_{\pi}-\pi_{\pi^*}$ belong to the B irreducible representation, while $\pi_{\pi}-\pi_{\pi^*}$ belong to A. These two excitations are symmetry-protected and cannot mix to form a superposition. Listed in Figure 3c, there is a contribution from higher energy excitations of same symmetry. These excitations into $\pi_{\pi^*}$ contribute less than 10% to the $S_0\rightarrow S_1$ and $S_0\rightarrow S_2$ transitions (see Figure S2 for method dependence).

As a consequence of their symmetry-protected helicity, properties relating to the electronic transitions will not be limited by the dual-helicity of MOs. The four $\pi \rightarrow \pi^*$ transitions have clear helicity associated to the change of electron density as shown in Figure 3c. The mixing of the two perpendicular $\pi$-systems is thus reflected in the electron density. This is the effect of the through-bond interaction mediated by the spiro-carbon, and it is a conclusive outcome of helical $\pi$-conjugation in spiroconjugated molecules.

All four electronic transitions have notable rotatory strengths, in particular the $S_0\rightarrow S_1$ and $S_0\rightarrow S_2$ transitions. Each pair of near-degenerate transitions have helical保护 in the change of electron density and opposite sign of the rotatory strength. The rotatory strength of each transition describes the difference in electron density and opposite sign of the rotatory strength. The degenerate transitions have opposite helicity in the change of rotation, so the two transition are not equally weighted linear combinations. Take the two lowest energy MO excitations; $\pi_{\pi}-\pi_{\pi^*}$ belong to the B irreducible representation, while $\pi_{\pi}-\pi_{\pi^*}$ belong to A. These two excitations are symmetry-protected and cannot mix to form a superposition. Listed in Figure 3c, there is a contribution from higher energy excitations of same symmetry. These excitations into $\pi_{\pi^*}$ contribute less than 10% to the $S_0\rightarrow S_1$ and $S_0\rightarrow S_2$ transitions (see Figure S2 for method dependence).

Figure 3. a) HOMO to LUMO+1 of spiropentadiene and S-1,4-dimethylspiropentadiene. b) Overview of their first four electronic transitions, and their symmetry designation. Electric-dipole ($\mu_{\pi,\pi^*}$) allowed transitions are in blue. c) Change of electron density for the $S_0\rightarrow S_1$, $S_0\rightarrow S_2$, $S_1\rightarrow S_2$ transitions of S-1,4-dimethylspiropentadiene. d) Simulated ECD spectrum of S-1,4-dimethylspiropentadiene and butadiyl-linked spiropentadiene. Oscillator strengths, $f$, are dimensionless. Rotatory strengths, $R$, in $10^{30}$ erg-esu-cm/Gauss. Depletion of density is in orange. Computed at the wB97X-D/Def2-TZVP level of theory.
We have made a brief assessment of the extent to which helical \( \pi \)-conjugation can also be present in larger spiroconjugated motives and tricyclic analogues.\(^{3^9}\) In spirononatetraene there are eight \( \pi \)-electrons and the MO symmetries differ from spiropentadiene. Though the HOMO-2 and HOMO-3 of dimethylspirononatetraene are clearly helical (Figure S9), they are less relevant for observable properties. Tricyclic spiroanalogues where the parent system has \( D_{2h} \) symmetry will also have similar mixing of its two \( \pi \)-systems. However, there will be additional nodal planes due to the extra \( \sigma \)-bonds (Figure S11 and S12).\(^{10, 11, 42}\) The electrohelicity effect thus appears to be less pronounced in larger systems.

In summary, we have explored how helical \( \pi \)-conjugation between the perpendicular \( \pi \)-systems of allene and spiropentadiene affect their electronic transitions and the helicity thereof. In allene the helicity of the \( \pi \)-MOs cancel out as all transitions are linear combinations of excitations involving MOs of both helicities. In spiropentadiene, the HOMO-1 and HOMO become helical in similar fashion to the \( \pi \)-mixing in allene, but the LUMO and LUMO+1 remain rectilinear \( \pi \)-MOs. The \( \pi \rightarrow \pi^* \) transitions are dominated by a single helical transition, and the MO symmetries and thus hold potential for spectroscopic verification of helical \( \pi \)-conjugation.

The authors thank Maria Fumanal (EPFL) for technical help with CASPT2 computations. MHG is grateful for funding from Independent Research Fund Denmark, case no. 9056-00009B.

Conflicts of interest

There are no conflicts to declare.

References

1. E. Soriano and I. Fernandez, Chem. Soc. Rev., 2014, 43, 3041-3105.
2. D. Wendinger and R. R. Tykwinski, Acc. Chem. Res., 2017, 50, 1468-1479.
3. M. H. Garner, R. Hoffmann, S. Rettrup and G. C. Solomon, ACS Cent. Sci., 2018, 4, 688-700.
4. H. Fischer and H. Kollmar, Theor. Chim. Acta, 1968, 12, 344-348.
5. H. E. Zimmerman, Acc. Chem. Res., 1971, 4, 272-280.
6. R. Heges, J. Org. Chem., 2015, 80, 11869-11876.
7. S. Honda, R. Sugawara, S. Ishida and T. Iwamoto, J. Am. Chem. Soc., 2021, 143, 2649-2653.
8. H. E. Simmons and T. Fukunaga, J. Am. Chem. Soc., 1967, 89, 5208-5215.
9. R. Hoffmann, A. Immamura and G. D. Zeiss, J. Am. Chem. Soc., 1967, 89, 5215-5220.
10. P. Bischof, R. Gleiter and R. Haider, J. Am. Chem. Soc., 1978, 100, 1036-1042.
11. R. Gleiter, R. Haider, J. Spanget-Larsen and P. Bischof, Tetrahedron Lett., 1983, 24, 1149-1152.
12. C. H. Hendon, D. Tiana, A. T. Murray, D. R. Carbery and A. Walsh, Chem. Sci., 2013, 4, 4278-4284.
13. A. Immamura and Y. Aoki, Chem. Phys. Lett., 2013, 590, 136-140.
14. T. Xu, J. H. Li, R. Momen, W. J. Huang, S. R. Kirk, Y. Shigeta and S. Jenkins, J. Am. Chem. Soc., 2019, 141, 5497-5503.
15. M. H. Garner and C. Corminboeuf, Org. Lett., 2020, 22, 8028-8033.
16. Y. Orimoto, Y. Aoki and A. Immamura, J. Phys. Chem. C, 2019, 123, 11134-11139.
17. M. H. Garner, A. Jensen, L. O. H. Hyllested and G. C. Solomon, Chem. Sci., 2019, 10, 4598-4608.
18. M. Caricato, J. Chem. Theory Comput., 2015, 11, 1349-1353.
19. M. D. Peeks, P. Neuhaus and H. L. Anderson, Phys. Chem. Chem. Phys., 2016, 18, 5264-5274.
20. A. Ozcelik, D. Aranda, S. Gil-Guerrero, X. A. Pola-Otero, M. Talaver, L. Wang, S. K. Behera, J. Gierschner, A. Peña-Gallego, F. Santoro, R. Pereira-Cameselle and J. L. Alonso Gómez, Chem. Eur. J., 2020, 26, 17342-17349.
21. M. H. Garner, W. Bro-Jørgensen and G. C. Solomon, J. Phys. Chem. C, 2020, 124, 18968-18982.
22. S. Gunasekaran and L. Venkataraman, J. Chem. Phys., 2020, 153, 124304.
23. P. Pinter and D. Munz, J. Phys. Chem. A, 2020, 124, 10100-10110.
24. F. A. Cotton, Chemical Applications of Group Theory, John Wiley & Sons, Inc., New York, 3rd edn., 1990.
25. A. Rauk, A. F. Drake and S. F. Mason, J. Am. Chem. Soc., 1979, 101, 2284-2289.
26. C. I. Elsevier, P. Vermeer, A. Gedanken and W. Runge, J. Am. Chem. Soc., 1985, 107, 2537-2547.
27. K. B. Wiberg, Y.-g. Wang, S. M. Wilson, P. H. Vaccaro, W. L. Jorgensen, T. D. Crawford, M. L. Abrams, J. R. Cheeseman and M. Luderer, J. Phys. Chem. A, 2008, 112, 2415-2422.
28. R. Gleiter and W. Schaefer, Acc. Chem. Res., 1990, 23, 369-375.
29. H. S. Rzepa and K. R. Taylor, J. Chem. Soc., Perkin Trans. 2, 2002, 1499-1501.
30. D. Hall and H. S. Rzepa, Org. Biomol. Chem., 2003, 1, 182-185.
31. M. C. Böhm and R. Gleiter, J. Chem. Soc., Perkin Trans. 2, 1979, 443-448.
32. J. P. Kenny, K. M. Krueger, J. C. Rienstra-Kiracofe and H. F. Schaefer, J. Phys. Chem. A, 2001, 105, 7745-7750.
33. W. E. Billups and M. M. Haley, J. Am. Chem. Soc., 1991, 113, 5084-5085.
34. R. K. Saini, V. A. Litosh, A. D. Daniels and W. E. Billups, Tetrahedron Lett., 1999, 40, 6157-6158.
35. T. Iwamoto, M. Tamura, C. Kabuto and M. Kira, Science, 2000, 290, 504.
36. Y. Guo, Z. Xia, J. Liu, J. Yu, S. Yao, W. Shi, K. Hu, S. Chen, Y. Wang, A. Li, M. Driess and W. Wang, J. Am. Chem. Soc., 2019, 141, 19252-19256.
37. A. de Meijere, A. F. Khlebnikov, R. R. Kostikov, S. I. Kozhushkov, P. R. Schreiner, A. Wittkopp and D. S. Yufit, Angew. Chem. Int. Ed., 1999, 38, 3474-3477.
38. C. Batich, E. Heilbroner, E. Rommel, M. F. Semmelhack and J. S. Foos, J. Am. Chem. Soc., 1974, 96, 7662-7666.
39. H. Dürr and R. Gleiter, Angew. Chem. Int. Ed. Engl., 1978, 17, 559-569.
40. J. Itatani, J. Levesque, D. Zeidler, H. Niikura, H. Pépin, J. C. Kieffer, P. B. Corkum and D. M. Villeneuve, Nature, 2004, 432, 867.
41. M. Wießner, D. Hauschild, C. Sauer, V. Feyer, A. Schöll and F. Reinert, Nat. Commun., 2014, 5, 4156.
42. J. Dressel, K. L. Chassey and L. A. Paquette, J. Am. Chem. Soc., 1988, 110, 5479-5489.
Supplementary Information for: Helical Electronic Transitions of Spiroconjugated Molecules

Marc H. Garner and Clemence Corminboeuf

Laboratory for Computational Molecular Design, Institute of Chemical Sciences and Engineering, Ecole Polytechnique federale de Lausanne (EPFL), 1015 Lausanne, Switzerland;
E-mail: clemence.corminboeuf@epfl.ch

Table of Contents

A. Computational Details S2
B. Change of Density Schematics S7
C. Cyclically-linked Molecules S10
D. Silicon and Germanium analogues S13
E. Spirononatetraene S15
F. Tricyclic Spiro-analogues S17
References S18
A. Computational Details

All molecular structures were optimized in their electronic ground state using density functional theory (DFT) at the at the ωB97X-D/Def2-TZVP level of theory using the Gaussian program package. Structural optimizations were completed according to the tight criteria. Integrals were evaluated on the ultrafine grid. Frequency analysis was done to ensure that all molecules have been optimized to local energy minima. All optimized structures are included as supporting files in xyz format. Molecular orbitals (MOs) and electron densities were rendered using Avogadro. MO were visualized with iso-value = 0.02, and densities with iso-value = 0.002 unless otherwise noted. Atomic orbitals were visualized using wxMacMolPlt. Excited-state computations were carried out using linear response time-dependent DFT at the ωB97X-D/Def2-TZVP level of theory as implemented in the Gaussian program package. Chiroptical properties were assessed using this method; for more detail on the approach for computing molecular optical activity we refer to the extensive reviews by Autschbach. All rotatory strengths reported were computed with velocity gauge representation. Conformation-resolved UV-Vis and electronic circular dichroism (ECD) spectra were generated using Gaussview by assuming a gaussian line-shape with the default parameter for the standard deviation, $\sigma=1/3099.6$ nm$^{-1}$. Details for the electronic transitions of allene, 1,3-dimethylallene, spiropentadiene, and 1,4-dimethylspiropentadiene are listed in Table S1-S4. Note that for $D_{2r}$-symmetry spiropentadiene the configuration interaction coefficients of the E transitions are meaningless due to the degeneracy of the transitions.

Table S1. $\pi \rightarrow \pi^*$ transitions of allene

| Transition | Configuration | E (eV) | Oscillator strength |
|------------|---------------|--------|--------------------|
| $S_0 \rightarrow S_4$ | $0.49 \cdot (\pi_y \rightarrow \pi_y^*) - 0.49 \cdot (\pi_x \rightarrow \pi_x^*)$ | 8.12 | 1.19 |
| $S_0 \rightarrow S_3$ | $0.50 \cdot (\pi_y \rightarrow \pi_y^*) + 0.50 \cdot (\pi_x \rightarrow \pi_x^*)$ | 7.50 | 0.00 |
| $S_0 \rightarrow S_2$ | $0.50 \cdot (\pi_x \rightarrow \pi_y^*) + 0.50 \cdot (\pi_y \rightarrow \pi_x^*)$ | 6.31 | 0.00 |
| $S_0 \rightarrow S_1$ | $0.50 \cdot (\pi_x \rightarrow \pi_y^*) - 0.50 \cdot (\pi_y \rightarrow \pi_x^*)$ | 6.08 | 0.00 |
### Table S2. $\pi \rightarrow \pi^*$ transitions of R-1,3-dimethylallene

| Transition | Configuration | E (eV) | Oscillator strength |
|------------|---------------|--------|---------------------|
| $S_0 \rightarrow S_4$ | $0.50 \cdot (\pi_M \rightarrow \pi_M^*) - 0.46 \cdot (\pi_P \rightarrow \pi_P^*)$ | 7.74 | 1.25 |
| $S_0 \rightarrow S_3$ | $0.49 \cdot (\pi_P \rightarrow \pi_M^*) - 0.49 \cdot (\pi_M \rightarrow \pi_P^*)$ | 7.27 | $0.3 \cdot 10^{-3}$ |
| $S_0 \rightarrow S_2$ | $0.49 \cdot (\pi_P \rightarrow \pi_M^*) + 0.49 \cdot (\pi_M \rightarrow \pi_P^*)$ | 6.19 | 0.00 |
| $S_0 \rightarrow S_1$ | $0.49 \cdot (\pi_M \rightarrow \pi_M^*) + 0.49 \cdot (\pi_P \rightarrow \pi_P^*)$ | 5.96 | 0.00 |

### Table S3. $\pi \rightarrow \pi^*$ transitions of spiropentadiene

| Transition | Configuration | E (eV) | Oscillator strength |
|------------|---------------|--------|---------------------|
| $S_0 \rightarrow S_4$ | $0.67 \cdot (\pi_y \rightarrow \pi_{x-y}^*) - 0.17 \cdot (\pi_y \rightarrow \pi_{x+y}^*)$ | 6.15 | $39.1 \cdot 10^{-3}$ |
| $S_0 \rightarrow S_3$ | $0.67 \cdot (\pi_x \rightarrow \pi_{x-y}^*) + 0.17 \cdot (\pi_x \rightarrow \pi_{x+y}^*)$ | 6.15 | $39.1 \cdot 10^{-3}$ |
| $S_0 \rightarrow S_2$ | $0.57 \cdot (\pi_y \rightarrow \pi_{x+y}^*) + 0.37 \cdot (\pi_x \rightarrow \pi_{x+y}^*)$ | 4.91 | $8.3 \cdot 10^{-3}$ |
| $S_0 \rightarrow S_1$ | $0.57 \cdot (\pi_x \rightarrow \pi_{x+y}^*) - 0.37 \cdot (\pi_y \rightarrow \pi_{x+y}^*)$ | 4.91 | $8.3 \cdot 10^{-3}$ |

### Table S4. $\pi \rightarrow \pi^*$ transitions of S-1,4-spiropentadiene

| Transition | Configuration | E (eV) | Oscillator strength |
|------------|---------------|--------|---------------------|
| $S_0 \rightarrow S_4$ | $0.67 \cdot (\pi_P \rightarrow \pi_{x-y}^*) + 0.18 \cdot (\pi_M \rightarrow \pi_{x-y}^*)$ | 6.12 | $67.6 \cdot 10^{-3}$ |
| $S_0 \rightarrow S_3$ | $0.67 \cdot (\pi_M \rightarrow \pi_{x-y}^*) + 0.18 \cdot (\pi_P \rightarrow \pi_{x-y}^*)$ | 6.12 | $70.7 \cdot 10^{-3}$ |
| $S_0 \rightarrow S_2$ | $0.67 \cdot (\pi_P \rightarrow \pi_{x-y}^*) - 0.18 \cdot (\pi_M \rightarrow \pi_{x-y}^*)$ | 5.02 | $11.9 \cdot 10^{-3}$ |
| $S_0 \rightarrow S_1$ | $0.67 \cdot (\pi_M \rightarrow \pi_{x-y}^*) - 0.18 \cdot (\pi_P \rightarrow \pi_{x-y}^*)$ | 5.02 | $12.0 \cdot 10^{-3}$ |
To test the findings using a multi-determinant wavefunction method, we use CASPT2 with cc-pVDZ basis set as implemented in the OpenMolcas 20.10 software suite.\textsuperscript{10-11} These computations were carried out primarily to verify how the excited states mix. The DFT-optimized structures were used for this purpose without further optimization. SCF MOs are visualized using MOLDEN.\textsuperscript{12}

Shown in Figure S1, an (8,8) active space was chosen for 1,3-dimethylallene covering the $\pi$-space and in part the $\sigma$-MOs relating to the methyl groups. In good qualitative agreement with the TD-DFT results, there is significant configuration interaction in the first four excited states, which involve excitation of orbitals of both helicities.

| $R$-1,3-dimethylallene | 8e/8o |
|-------------------------|-------|
| **CAS-SCF**             |       |
| cc-pvdz                 |       |
| MOs ($C_2$)             |       |
| $4a^*$                  | $4b^*$|
| $3a^*$                  | $3b^*$|
| $2a$                    | $2b$  |
| $1a$                    | $1b$  |

| $S_0$ (0.0 eV):         | 92% SCF ground-state |
| $S_1$ (B) 6.2 eV:       | 45% $2b\rightarrow 3a^*$, 42% $2a\rightarrow 3b^*$ |
| $S_2$ (A) 6.7 eV:       | 53% $2a\rightarrow 3a^*$, 36% $2b\rightarrow 3b^*$ |
| $S_3$ (A) 7.7 eV:       | 32% $2a\rightarrow 3a^*$, 50% $2b\rightarrow 3b^*$ |
| $S_4$ (B) 8.9 eV:       | 41% $2b\rightarrow 3a^*$, 43% $2a\rightarrow 3b^*$ |

**Figure S1.** CASPT2 (8,8) computation of first four excited states of dimethylallene. Configurations contributing less than 4% are not listed.
Shown in Figure S2, an (12,8) active space was chosen for 1,4-dimethylspiropentadiene covering the π-space in part the σ-MOs relating to the methyl groups. In good qualitative agreement with the TD-DFT results and the symmetry restrictions, there is only interaction between configuration of same symmetry. Consequently, the first four excited states do not involve near-degenerate orbitals of both helicities, only minor contributions of higher/lower energy excitations.

**Figure S2.** CASPT2 (12,8) computation of first four excited states of dimethylspiropentadiene. Configurations contributing less than 4% are not listed.
Shown in Figure S3, an (8,8) active space was chosen for 1,4-dimethylspiropentadiene covering the $\pi$-space. Similar to dimethylspiropentadiene, there is good qualitative agreement with the TD-DFT results and the symmetry restrictions, there is only interaction between configuration of same symmetry. There is only minor configuration interaction from higher/lower energy excited states, which contribute few percent to the first four excited states.

**Figure S3.** CASPT2 (8,8) computation of first four excited states of dimethylspirononatetraene. Configurations contributing less than 4% are not listed.
B. Change of Density Schematics

We are interested in understanding the patterns of $\Delta \rho$ which is appears in from ab initio computations. To assess this, we schematically draw up each type of occupied MO ($\pi_x, \pi_y, \pi_M, \pi_p$) and unoccupied MO ($\pi_x^*, \pi_y^*, \pi_M^*, \pi_p^*$). Given the unoccupied $\pi$-MOs will have one extra nodal plane, we can schematically predict the qualitative depletion of electron density. In helical MOs the extra nodal plane is expressed as extra torsion along the helical axis. This torsion is quite systematic, and we refer to earlier work for a detailed assessment.\textsuperscript{13}

In Figure S4, this assessment is carried out for allene. As one may expect, any single excitation from a linear to higher energy linear MO yields a linear change of density. A superposition of two such excitations will also be linear. Moving on to excitations between helical MOs, excitations from a helical to a higher energy helical MO gives a helical change if both MOs have same helicity; if they have opposite helicity there will be a helical sense of direction without forming a continuous helical pattern (a broken helix). A superposition of helical excitations will return to a linear change of density because certain regions have opposing change of density. From an MO perspective this is also quite intuitive because the helical MOs are formed as a linear combination of two linear MOs, which is symmetry-protected in $C_2$-symmetry 1,3-dimethylallene.\textsuperscript{13} Taking again the linear combinations of two excitations of helical MOs returns us to the linear MO picture.

In spiropentadiene, the excitations are from an occupied helical $\pi$-MO into an unoccupied linear MO. The four different excitations are shown in Figure S5. Please note it is inherently difficult to draw this change; in accordance with the symmetry-adaptation to the C2 point group of the substituted molecule, the p-orbital (and the density it provides) on the central spiro-carbon are rotated $\pm 45^\circ$ relative to the two planes of the molecule. All four excitations yield a helical change of density, in agreement with the TD-DFT computations presented in the manuscript.
Figure S4. Schematic overview of the density change in allenes. Depletion of density is shown in orange.
Figure S5. Schematic overview of the density change in spiropentadiene. Depletion of density is shown in orange.
C. Cyclically-linked Molecules

Due to the structural similarity to cyclohexane, 1,3-butadiylallene assumes a chair and a twist-boat conformation. These are shown in Figure S6 along with the frontier MOs. The twist conformer is found to be slightly more stable than the chair by 33 meV.

The helical MOs are significantly changed compared to dimethylallene and consequently the electronic transitions change in 1,3-butadiylallene. Shown in the simulated ECD spectrum in Figure S6b, multiple transitions give rise to optical activity. We speculate this is related to the changed MO contributions to the electronic transitions (figure S6c). The change of electron density is helical in \( S_0 \rightarrow S_2 \), and \( S_0 \rightarrow S_3 \), with opposite sign depending on the helicity. \( S_0 \rightarrow S_4 \) is not a \( \pi \rightarrow \pi^* \) transition as other close-lying MOs mix into the transition.

1,3-butadiylspiropentadiene has same two conformations as the butadiylallene; however, only chair conformer is most relevant as it is 55 meV lower energy than the twist conformer. For completeness, we include both conformers in the overview in Figure S7. The helical HOMO and HOMO-1 are energetically split in 1,3-butadiylspiropentadiene and consequently the electronic transitions change. As the electronic transitions are energetically split, the rotatory strength gives rise to big \( \Delta \epsilon \) in the simulated ECD spectrum in Figure S7b. The helicity of the electronic transition is almost lost in the change of density in cases where the MO excitations mix almost equally.
Figure S6. a) Frontier MOs of 1,3-dimethylallene and cyclically linked 1,3-butadiyllallene. b) Simulated UV-Vis and ECD. Transitions are marked by their final state. c) Change of electron density of R-1,3-butadiyllallene for the $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, and $S_0 \rightarrow S_3$ electronic transitions computed at the oB97X-D/Def2-TZVP level of theory. Oscillator strengths, $f$, are dimensionless. Rotatory strengths, $R$, are in $10^{40}$ erg·esu·cm/Gauss. Depletion of density is in orange. Iso-value = 0.002.
Figure S7. a) Frontier MOs of 1,4-dimethylspiropentadiene and cyclically-linked 1,4-butadiylspiropentadiene b) Simulated UV-Vis and ECD spectra. Transitions are marked by their final state. c) Change of electron density of S-1,4-butadiylspiropentadiene for the $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_4$ electronic transitions computed at the ωB97X-D/Def2-TZVP level of theory.\(^1\)\(^2\) Oscillator strengths, $f$, are dimensionless. Rotatory strengths, $R$, are in $10^{-40}$ erg-esu·cm/Gauss. Depletion of density is in orange. Iso-value = 0.002.
D. Silicon and Germanium analogues

The silicon and germanium analogues of spiropentadiene have similar molecule structure to the carbon system, and the same symmetry arguments apply. For simplicity we have chosen to use the same substituents as in the carbon system, although larger substituents are typically used synthetically to improve the kinetic stability of the compounds.

The main difference between spiropentadiene and its sila- and germa-analogues, is that there are $\sigma$-MOs that are close to the HOMO-LUMO gap, which mix significantly into the $\pi-\pi^*$ transitions. Furthermore, the helical $\pi$-MOs have less weight on the central spiro-carbon.

Listed in Figure S8b, the transitions helicity is to some extend preserved in $S_0\rightarrow S_1$ and $S_0\rightarrow S_2$, but is largely lost in $S_0\rightarrow S_3$ and $S_0\rightarrow S_4$ where multiple MO excitations contribute. It is clear that the electronic transitions can be helical in substituted spiropentasiladienes and spiropentagermadienes, but they are more liable to mixing of excitations involving $\sigma$-MOs. This may also depend on the choice of substituents.
Figure S8. HOMO-1 to LUMO+3 of dimethylspiropentasiladiene and dimethylspiropentagermaadiene computed at the oB97X-D/Def2-TZVP level of theory. The MOs are shown with an Iso-value = 0.01. b) Overview of S₀→S₁ to S₀→S₄ electronic transitions and their symmetry designations, and computed change of electron. Oscillator strengths, f, are dimensionless. Rotatory strengths, R, are in 10⁴⁰ erg·esu·cm/Gauss). Depletion of density is in orange. Iso-value = 0.001.
E. Spirononatetraene

Like spiropentadiene and allene, spirononatetraene has $D_{2d}$ symmetry.\textsuperscript{14-15} While its electronic structure is similar to spiropentadiene, spirononatetraene has four more $\pi$-electrons and therefore the MO symmetries switch. Thus the HOMO-2 and HOMO-3 ($\pi_x$ and $\pi_y$), and the LUMO and LUMO+1 ($\pi_x$ and $\pi_y$) are degenerate, while the HOMO and HOMO-1 ($\pi_{x+y}$ and $\pi_{x-y}$) are non-degenerate and delocalize via through-space overlap, as shown in Figure S8. Upon disubstitution the HOMO-2 and HOMO-3 ($\pi_p$ and $\pi_M$) mix and show clear helicity. The LUMO and LUMO+1 ($\pi_p^*$ and $\pi_M^*$) also become helical, which can be seen by close inspection of the nodal planes (there are none between the two $\pi$-systems). However, their much sharper twist means the helicity is less obvious. The HOMO-2 and HOMO-3 ($\pi_p$ and $\pi_M$) are clearly helical, but will be less relevant for observable properties. An overview of the electronic transitions are provided in Figure S9. Most of the helicity is lost in the transitions due to the weak helicity in ($\pi_p^*$ and $\pi_M^*$).

![Figure S9](image_url)

Figure S9. HOMO-3 to LUMO+1 of spirononatetraene and $S$-2,7-dimethylspirononatetraene computed at the $\omega$B97X-D/Def2-TZVP level of theory.\textsuperscript{1-2}
Figure S10. a) Overview of $S_0 \rightarrow S_1$ through $S_0 \rightarrow S_4$, and $S_0 \rightarrow S_7$ and $S_0 \rightarrow S_8$ electronic transitions of spirononatetraene and $S$-$2,7$-dimethylspirononatetraene, and their symmetry designations. Electric-dipole allowed transitions are marked in blue. b) Change of electron density for the $S_0 \rightarrow S_1$ through $S_0 \rightarrow S_4$, and $S_0 \rightarrow S_7$ and $S_0 \rightarrow S_8$ electronic transitions of $S$-$2,7$-dimethylspirononatetraene. Oscillator strengths, $f$, are dimensionless. Rotatory strengths, $R$, are in $10^{40}$ erg esu cm/Gauss. Depletion of density is in orange. Iso-value = 0.001.
F. Tricyclic Spiro-analogues

**Figure S11.** HOMO-1 to LUMO+1 of spiro-analogues tricyclooctadiene and dimethyltricyclooctadiene computed at the ωB97X-D/Def2-TZVP level of theory.\textsuperscript{1,2}

**Figure S12.** HOMO-3 to LUMO+1 of spiro-analogues tricyclododecatetraene and dimethyl tricyclododecatetraene computed at the ωB97X-D/Def2-TZVP level of theory.\textsuperscript{1,2}
REFERENCES

1. Chai, J.-D.; Head-Gordon, M. Long-Range Corrected Hybrid Density Functionals with Damped Atom–Atom Dispersion Corrections. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615-6620.

2. Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.

3. M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox *Gaussian 16, Revision A.03*, Gaussian, Inc., Wallingford CT: 2016.

4. Hanwell, M. D.; Curtis, D. E.; Lonie, D. C.; Vandermeersch, T.; Zurek, E.; Hutchison, G. R. Avogadro: An Advanced Semantic Chemical Editor, Visualization, and Analysis Platform. *Journal of Cheminformatics* **2012**, *4*, 17.

5. [http://avogadro.cc/](http://avogadro.cc/) Avogadro: An Open-Source Molecular Builder and Visualization Tool. Version 1.2.0, 2020.

6. Bode, B. M.; Gordon, M. S. Macmolplt: A Graphical User Interface for Gamess. *Journal of Molecular Graphics and Modelling* **1998**, *16*, 133-138.

7. Autschbach, J. Computing Chiroptical Properties with First-Principles Theoretical Methods: Background and Illustrative Examples. *Chirality* **2009**, *21*, E116-E152.

8. Srebro-Hooper, M.; Autschbach, J. Calculating Natural Optical Activity of Molecules from First Principles. *Annu. Rev. Phys. Chem.* **2017**, *68*, 399-420.

9. Denningen, R.; Keith, T. A.; Millam, J. M. *Gaussview, Version 6.1*, Semichem Inc., Shawnee Mission, KS: 2016.

10. Fdez. Galván, I.; Vacher, M.; Alavi, A.; Angeli, C.; Aquilante, F.; Autschbach, J.; Bao, J. J.; Bokarev, S. I.; Bogdanov, N. A.; Carlson, R. K., et al. Openmolcas: From Source Code to Insight. *J. Chem. Theory Comput.* **2019**, *15*, 5925-5964.

11. Aquilante, F.; Autschbach, J.; Baiardi, A.; Battaglia, S.; Borin, V. A.; Chibotaru, L. F.; Conti, I.; De Vico, L.; Delcey, M.; Fdez. Galván, I., et al. Modern Quantum Chemistry with [Open]Molcas. *J. Chem. Phys.* **2020**, *152*, 214117.

12. Schaffenaar, G.; Noordik, J. H. Molden: A Pre- and Post-Processing Program for Molecular and Electronic Structures*. *J. Comput. Aided Mol. Des.* **2000**, *14*, 123-134.

13. Garner, M. H.; Hoffmann, R.; Rettrup, S.; Solomon, G. C. Coarctate and Möbius: The Helical Orbitals of Allene and Other Cumulenes. *ACS Cent. Sci.* **2018**, *4*, 688-700.

14. Haselbach, E.; Allan, M.; Bally, T.; Bednarek, P.; Sergenten, A.-C.; de Meijere, A.; Kozhushkov, S.; Piacenza, M.; Grimme, S. Spiro[4.4]Nonatetraene and Its Positive and Negative Radical Ions: Molecenran Structure Investigations. *Helv. Chim. Acta* **2001**, *84*, 1670-1693.
15. Sowa, J. K.; Mol, J. A.; Briggs, G. A. D.; Gauger, E. M. Spiro-Conjugated Molecular Junctions: Between Jahn–Teller Distortion and Destructive Quantum Interference. *J. Phys. Chem. Lett.* **2018**, *9*, 1859-1865.
| Other files |
|-------------|
| xyz_files_v3.zip (8.44 KiB) | view on ChemRxiv | download file |