

# Three Distinct Torsion Profiles of Electronic Transmission through Linear Carbon Wires

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Electronic Transmission, Single-molecule Conductance, Axial torsion, carbyne, polyyne, cumulene, carbon wire, helical molecular orbitals.

**ABSTRACT.** The one-dimensional carbon allotrope carbyne, a linear chain of *sp*-hybridized carbon atoms, is predicted to exist in a polyynic and a cumulenic structure. While molecular forms of carbyne have been extensively characterized, the structural nature is hard to determine for many linear carbon wires that are made in-situ during pulling experiments. Here, we show that cumulenes and polyynes have distinctively different low-bias conductance profiles under axial torsion. We analyze the change of the electronic structure, Landauer transmission, and ballistic current density of the three types of closed-shell molecular carbynes as a function of the torsion angle. Both polyynic, odd-carbon cumulenic, and even-carbon cumulenic carbon wires exhibit helical frontier molecular orbitals when the end-groups are not in a co-planar configuration. This helical conjugation effect gives rise to strong ring current patterns around the linear wires. Only the transmission of even-carbon polyynic wires follows the well-known cosine-squared law with

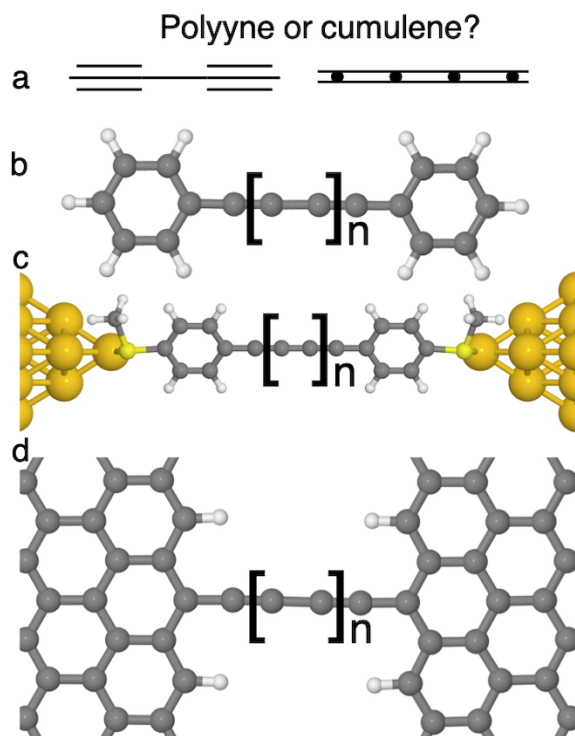
axial torsion that is also seen in biphenyl-type systems. Notably, the transmission of even-carbon cumulenic carbon wires rises with axial torsion from co-planar towards perpendicular orientation of the end-groups. The three distinct transmission profiles of polyyynes, odd-carbon cumulenes, and even-carbon cumulenes may allow for experimental identification of the structural nature of linear carbon wires. Their different electron transport properties under axial torsion furthermore underline that, in the molecular limit of carbyne, three different subclasses of linear carbon wires exist.

## INTRODUCTION

The elusive one-dimensional carbon allotrope carbyne attracts much interest due to a number of proposed properties that may be desirable for materials and molecular electronics.<sup>1-2</sup> Depicted in Figure 1a, carbyne is a linear chain of *sp*-hybridized carbon atoms and exists in two configurations: The polyynic type with bond-length alternation, and the cumulenic type with equal bond lengths. The specific properties depend on the type of carbyne; for example, polyynic carbyne is predicted to be a semiconductor while cumulenic carbyne is metallic.<sup>3-8</sup> However, as inferred by the ball-and-stick models in Figure 1, when bond lengths cannot be determined it is fundamentally difficult to assess the polyynic or cumulenic nature of carbon wires.

Molecular carbon wires have attracted broad interest as model systems for carbyne, and both polyyynes and cumulenes of substantial length have been reported.<sup>9-13</sup> These molecular wires, exemplified in Figure 1b, have the advantage that their structure and properties can be analyzed with the spectroscopic tools of modern chemistry.<sup>2, 12-13</sup> However, their properties may not fully reflect that of extended structures. Illustrated in Figure 1c, an extended carbyne system can be formed by letting the molecule bridge a nanoscale gap between to metal electrodes. The electron

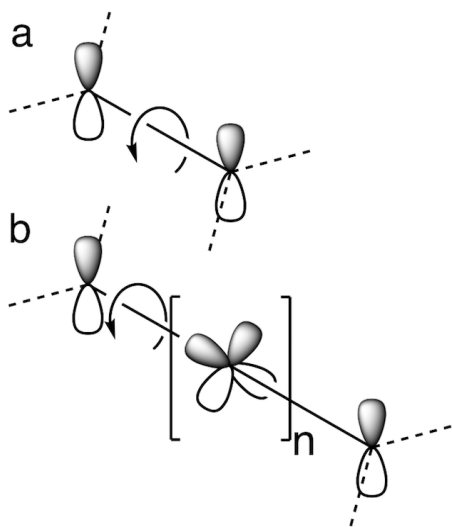
transport properties of several short molecular carbynes have been examined experimentally in single-molecule junctions for both polyyenic and cumulenenic molecular wires.<sup>14-20</sup> In single-molecule junctions the chemical structure of the isolated molecule is typically retained, and therefore the polyyenic or cumulenenic configuration of the molecular wire can be controlled by chemical design. A third type of carbyne-like system is illustrated in Figure 1d. Linear carbon wires have been made experimentally by pulling from carbon-based electrodes or inside carbon nanotubes.<sup>21-27</sup> However, the properties of these out-of-equilibrium carbon wires produced in-situ during pulling experiments are somewhat elusive, and the polyyenic or cumulenenic nature of the wires is not straightforward to identify.<sup>1</sup> Given these wires are still within the molecular limit of carbyne (lengths of tens or few hundreds of atoms), we suggest that axial torsion of extended carbon wires is a reliable way to distinguish the two (or three) types of carbyne structures from each other.



**Figure 1.** a) Polyyenic and cumulenenic Kekulé structures of carbyne. b) Ball-and-stick model of a molecular carbyne wire. c) Ball-and-stick model of a functionalized molecular carbyne bridging

two metal electrodes in a single-molecule junction. d) Ball-and-stick model of an extended carbon structure with a carbyne unit bridging two carbon-based electrodes, e.g., graphene.

**AXIAL TORSION OF MOLECULES.** Axial torsion is a fundamental degree of freedom in many molecules and has been studied extensively in the context of molecular electronics. The low-bias single-molecule conductance of a functionalized biphenyl molecule follows a cosine-squared law of the dihedral angle between the two benzene rings.<sup>28-32</sup> This dependence follows directly from the overlap integral of two p-orbitals on adjacent atoms, which has a cosine dependence on the dihedral angle between the two orbitals as sketched in Figure 2a. In any molecule where two otherwise separate  $\pi$ -systems couple directly through a single  $\pi$ -interaction, we expect to see the cosine-squared dependence in the off-resonant electronic transmission as a function of the torsion dihedral angle. Biphenyl is perhaps the most studied example of such a situation.<sup>33-35</sup>



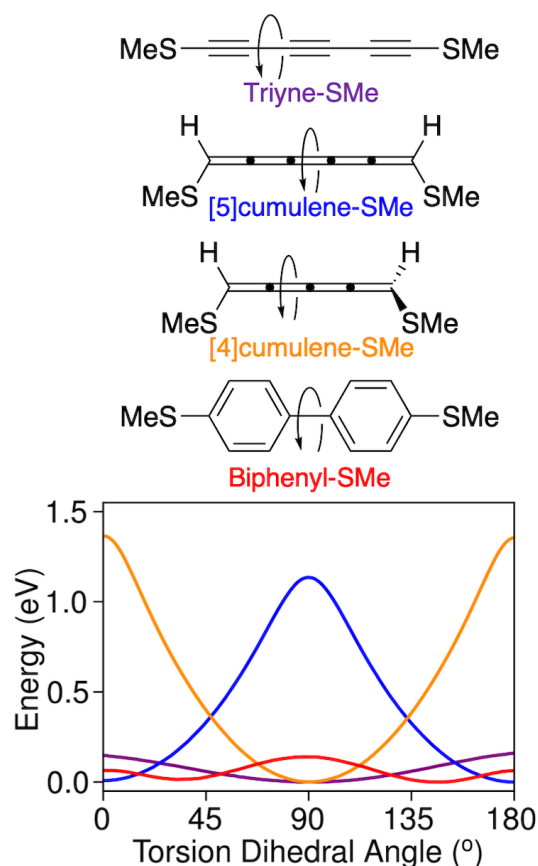
**Figure 2.** Two simplified cases of coupling between two p-orbitals during axial torsion. a) direct coupling through a single  $\pi$ -bond, e.g. the case of biphenyl. b) Coupling mediated by a coarctate orbital-system, e.g., a polyyenic or cumulenenic carbon bridge of arbitrary length.

Now we extend the first case into a system where two  $\pi$ -systems couple through a linear  $sp$ -hybridized carbon bridge. As illustrated in Figure 2b, a fundamental difference is apparent from the system shown in Figure 2a. The two terminal  $\pi$ -systems can couple through what may be considered as two orthogonal  $\pi$ -systems on the linear carbon bridge. However, the orbital system on the linear carbon bridge can be oriented in any way, and can be depicted as a continuously overlapping cyclic p-orbital basis as illustrated in Figure 2b.<sup>36-38</sup> In this “coarctate” orbital basis there is an unbroken overlap through the carbon wire that connects the two terminal  $\pi$ -systems even when they are rotated 90° relative to each other. This coarctate orbital topology appears in linear carbon molecules of both the polyynic and cumulenic type, and we recently described this in detail.<sup>39</sup>

In the molecular orbital picture, the possibility of electronic coupling between perpendicular end-groups of an  $sp$ -hybridized carbon wire manifests itself in the form of helical molecular orbitals that span the entire length of the linear carbon bridge.<sup>39-46</sup> Such helical  $\pi$ -orbitals appear in linear carbon wires upon a suitable reduction of symmetry due to substituents or axial torsion. Consequently, a molecule can be single-handed chiral while orbitals of both helicities appear; this has serendipitously been shown for a number of linear molecular systems.<sup>47-53</sup> Despite having perpendicular end-groups in their ground-state structure, odd-carbon cumulenes with pyramidalized single-faced  $\pi$ -donor substituents can achieve high electronic transmission similar to that of even-carbon cumulenes and polyynes.<sup>45, 54</sup> Furthermore, helical  $\pi$ -orbitals can give rise to ring currents around the linear wire where the circular direction of the current is controlled by the helicity of the frontier orbitals. The understanding of the relation between helical molecular orbitals, electronic transmission, and ring currents in linear systems is still in its infancy.<sup>45, 55</sup>

Motivated by the insight local pictures of ballistic current provide for aromatic hydrocarbons,<sup>56-61</sup> we will address this issue further in this study.

**MOLECULAR CARBYNES.** In the molecular limit of carbyne, there are not only two, but three types of stable closed-shell molecules. Closed-shell polyynes only exist as even-carbon systems with alternating single and triple bonds. Like in biphenyl systems, there is almost free rotation for the end-groups of polyynic wires as exemplified by the torsion energy profile in Figure 3 and Figure S1. Cumulenes exist both as even- and odd-carbon closed-shell systems; for the remainder of the manuscript we will adhere to the chemical nomenclature and refer to them as even- $n$  and odd- $n$  [ $n$ ]cumulenes, where  $n$  is the number of cumulenenic double bonds (the number of carbon atoms is thus  $n+1$ ).<sup>13</sup> Odd- $n$  cumulenes have co-planar end-groups in their ground-state structure with considerable torsion barriers.<sup>20, 62-66</sup> As shown in Figure 3, even- $n$  cumulenes have similar torsion barriers, however, the end-groups are perpendicular in the ground-state structure where the molecules have a closed-shell electronic structure. This remarkable structural difference between the odd- $n$  and even- $n$  cumulenes means that they are almost as different from each other as they are to polyynes. Although the electronic and transport properties of closed-shell cumulenes and polyynes have been described extensively in the literature,<sup>6-8, 43, 54, 67-70</sup> the structural differences between odd- $n$  and even- $n$  cumulenes has been overlooked in the charge transport literature and has been interpreted as an odd-even effect.<sup>3-5, 71-83</sup> We will argue such an interpretation is not meaningful in the molecular limit of carbyne, as we demonstrate in this work that the charge transport properties of the two cumulene types are fundamentally different.



**Figure 3.** Axial torsion energy profile of three types of thiomethyl-functionalized linear carbon wires and the equivalent biphenyl.

In this article we revisit axial torsion of polyynic and cumulenic carbon wires and analyze the electronic structure, Landauer transmission, and ballistic current density of thiomethyl-functionalized **triyne-SMe**, **[5]cumulene-SMe**, and **[4]cumulene-SMe** illustrated in Figure 3, as well as the equivalent **biphenyl-SMe**. We apply our recently developed s-band electrode transmission code,<sup>84</sup> which allow for realistic coupling into the contact groups with only a minimal perturbation of the electronic structure of the molecule thereby allowing us to draw general conclusions.

The article is structured as follows. In the following three sections we present the results for each of the three molecular types of carbyne: polyynic, odd- $n$  cumulenic, and even- $n$  cumulenic. After a brief introduction of each type of wire, each section covers the change of the electronic structure and electron transport properties during axial torsion. We identify three distinct torsion profiles for the low-bias single-molecule conductance, supporting the view molecular carbynes must be considered as three distinct classes of closed-shell carbon wires: polyynes, odd- $n$  cumulene, and even- $n$  cumulene. Before concluding on the findings, we provide a discussion of the theoretical approach and its possible limitations.

## POLYYNIC CARBON WIRES

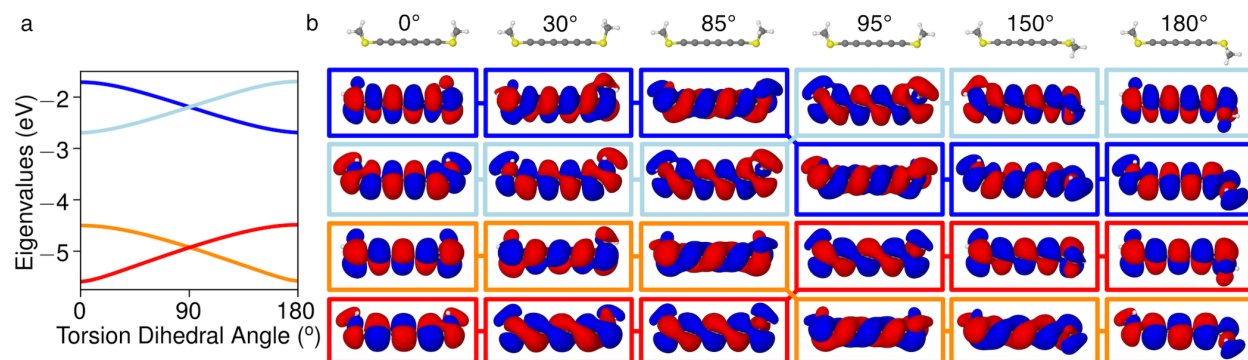
Polyynes are linear chains of  $sp$ -hybridized carbon where the bonds formally alternate between single and triple bonds, and accordingly there is a low torsion barrier in such molecules as exemplified in Figure 2. The strong bond-length alternation opens the HOMO-LUMO gap, and contributes to making polyynes more stable than cumulenes of equivalent length. With reasonable kinetic and thermodynamic stability, the single-molecule conductance of polyynes has been measured experimentally in single-molecule junctions as long as a hexyne (a 14 atom long linear carbon molecule).<sup>14-18</sup>

**ELECTRONIC STRUCTURE.** Shown in Figure 4, four frontier molecular orbitals and their eigenvalues are calculated for the **triyne-SMe**. The two  $\pi$ -orbital systems are separated by symmetry when end-groups are co-planar at  $0^\circ$  and  $180^\circ$ , and the  $\pi$ -orbitals take their normal rectilinear shape. The shape of the molecular orbitals immediately changes towards a helical shape when the end-groups are rotated into a non-planar geometry because the symmetry of the molecule is reduced. This is the helicogenic symmetry ( $C_2$  or  $D_2$ ) we have previously identified.<sup>39</sup> Polyynes



with non-planar end-groups will exhibit some degree of helical molecular orbitals due their helicogenic symmetry, and a number of such molecules have already been synthesized.<sup>85-89</sup>

Starting from 0° in Figure 4 we can trace the gradual evolution of the molecular orbitals. The two orbital pairs (HOMO–1 and HOMO, LUMO and LUMO+1) are each separated in energy by ~1 eV. As the molecule is twisted towards 90° the energy separation between in each orbital pair decreases and the HOMO-LUMO gap becomes slightly larger. At 30° the helicity of each molecular orbital is visually clear. The HOMO (orange in Figure 4) is a minus helix and as we apply a clockwise torsion of the molecule this helix is being unwound, and consequently its eigenvalue decreases. The HOMO–1 (red in Figure 4) is a plus helix and consequently it is being overwound with the torsion of the molecule and its eigenvalue increases. As the eigenvalues change in opposite directions the HOMO–1 and HOMO “switch place” at 90°, as do the LUMO and LUMO+1. From 90° to 180° the energy splitting of the two orbital pairs is recovered and the HOMO-LUMO equivalently becomes smaller. Finally, at 180° the original  $\pi$ -orbitals are recovered as the HOMO (orange) has been changed into an orbital equivalent to the original HOMO–1 (red) and vice-versa. By visual inspection it is clear from Figure 4 that the molecular orbitals appear more helical close to 90°; we are working towards quantifying this orbital helicity in future work.

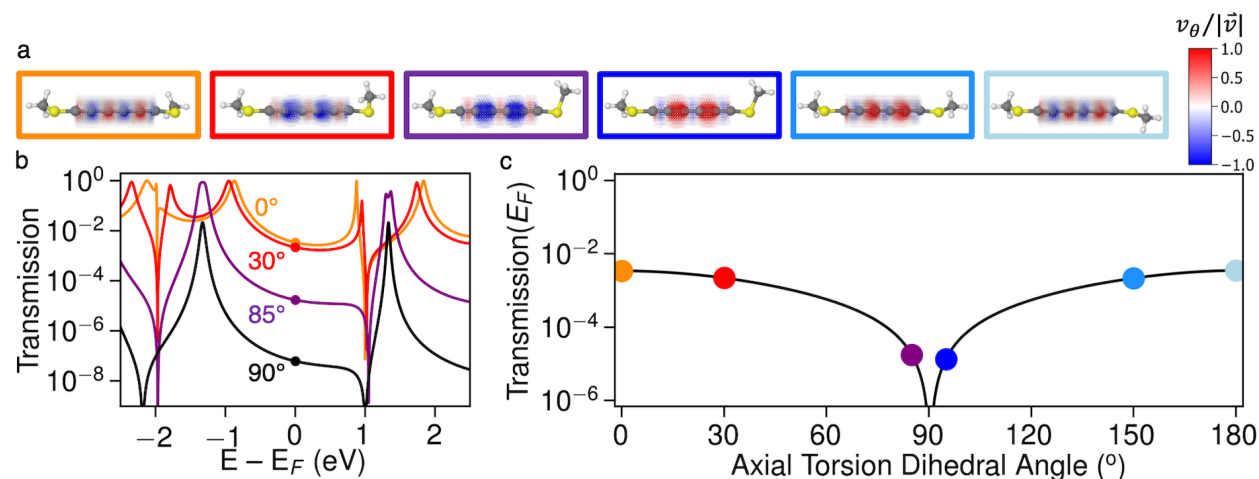


**Figure 4.** Change of the frontier molecular orbitals of **triyne-SMe** under axial torsion. a) Eigenvalues of the frontier molecular orbitals plotted as a function of dihedral angle. b) Iso-plot of the four frontier molecular orbitals at dihedral angles of 0°, 30°, 85°, 95°, 150°, and 180°, the molecular structures are shown at the top, followed by the LUMO+1, LUMO, HOMO, and HOMO–1 at the bottom.

ELECTRON TRANSPORT. Shown in Figure 5, the current density and electronic transmission is calculated for **triyne-SMe** under axial torsion. With co-planar end-groups the current follows a largely linear path (arrows are almost white due to the small  $\theta$ -component, see also Figure S17 and S20) as we may expect for a linear  $\pi$ -system. As torsion is applied ring currents become increasingly clear around the wire. As can be seen in Figure 5a, at 0° and 180° torsion weak ring currents are centered at the carbon atoms. At 85° and 95° torsion strong ring currents are centered around the two formal single-bonds of the carbon wire, see also Figure S18 and S19. The direction of the circular component of the current reverses at 90°, which can be observed by the change of the color of the arrows from blue to red. It is at 90° that the helicity of the HOMO and LUMO changes because of the torsion (see Figure 4), underlining the correlation between the helicities in the electronic structure and the direction of the ballistic ring currents.

At 0° and 180° the transmission is high, as we may expect from having a fully  $\pi$ -conjugated transport path through the molecule. Shown in Figure 5b and 5c, the transmission is effectively suppressed by axial torsion towards 90°, and follows a  $\cos^2$  dependence like **biphenyl-SMe**. This large transmission difference by torsional control of the end-groups has previously been suggested as a means to achieve electronic functionality in polyyne-based molecular devices.<sup>90-93</sup> The suppression happens as the HOMO and HOMO–1 (LUMO and LUMO+1) become degenerate at ~90° (see Figure 4), and consequently the transmission through the helical  $\pi$ -systems is fully

suppressed. We can consider this as a destructive quantum interference effect due to the two helical orbital symmetries.<sup>45, 94-98</sup> The reversal of ring currents at 90° is also intimately linked to this interference effect.<sup>45, 56</sup> The full transmission plots at 95°, 150° and 180° are almost identical to those at 85°, 30°, and 0° and are shown in Figure S4.



**Figure 5.** Current density and transmission of **triyne-SMe** under axial torsion. a) Current density calculated at the Fermi energy colored by the normalized  $\theta$  vector component at dihedral angles (from left to right) 0°, 30°, 85°, 95°, 150°, and 180°. The current density vector field is plotted as arrows that are normalized in each plot; each arrow is colored by its circular vector component ( $v_\theta$ ) normalized relative to its total vector length. High resolution images are included in SI part H. b) Transmission plotted semilogarithmically against energy at select dihedral angles. c) Transmission at the fermi energy plotted against the torsion dihedral angle.

## ODD-*n* CUMULENIC CARBON WIRES

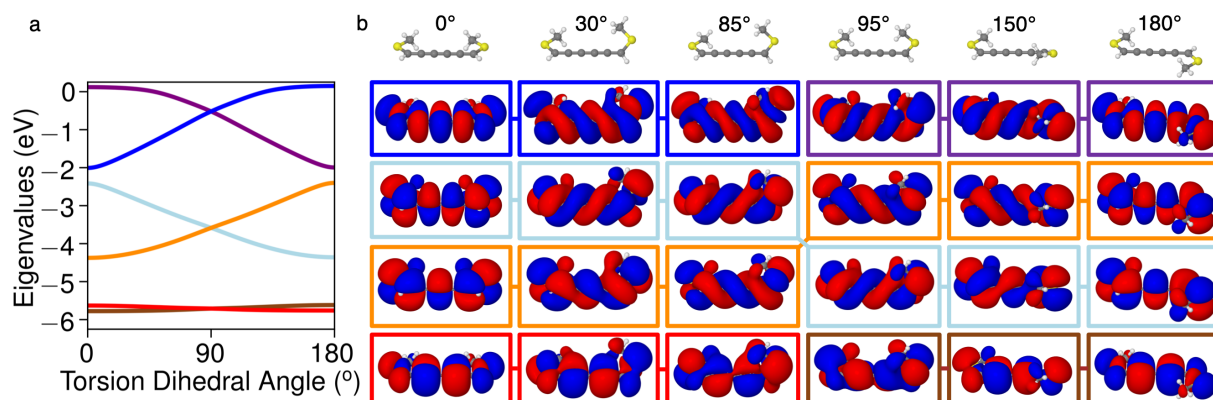
Cumulenes are linear chains of *sp*-hybridized carbon with consecutive formal double-bonds and consequently there is almost no bond-length alternation.<sup>13</sup> Like polyynes, odd-*n* cumulenes have an even number of carbon atoms in the linear chain. Consequently, odd-*n* cumulenes have co-

planar end-groups in their closed-shell ground-state structure (see Figure 3). Although less stable than polyynes, [9]cumulenes have been characterized, and functionalized [3]- and [5]cumulenes have been measured in single-molecule junction experiments.<sup>13, 19-20</sup> The single-molecule conductance of odd- $n$  cumulenes is expected to be higher than that of equivalent polyynes due to the smaller bond-length alternation, which narrows the HOMO-LUMO gap.<sup>54</sup>

**ELECTRONIC STRUCTURE.** The four frontier molecular orbitals and their eigenvalues are calculated for the **[5]cumulene-SMe** in Figure 6. At 0° and 180°, the two  $\pi$  orbital systems are separated by symmetry because the end-groups are co-planar, and the  $\pi$  orbitals take their usual rectilinear shape. The two  $\pi$ -systems are non-degenerate as the in-plane  $\pi$ -system spans only four carbon atoms, while the out-of-plane  $\pi$ -system spans all six carbon atoms. As with the polyynes, the shape of the molecular orbitals immediately changes towards a helical shape when the end-groups are rotated into a non-planar geometry because the symmetry of the molecule is reduced and a helicogenic symmetry is achieved.<sup>39, 43</sup>

Starting from 0° in Figure 6, we can trace the gradual evolution of the molecular orbitals. Starting out at 0°, each of the two orbital pairs (HOMO–1 and HOMO, LUMO and LUMO+1) are close in energy. Under torsion the HOMO-LUMO gap rapidly narrows and at 90° the HOMO and LUMO become degenerate and cross. The frontier molecular orbitals of the non-planar molecules have clear helicity, which changes at 90°. Shown in Figure 6b, the HOMO and LUMO (light-blue and orange in Figure 6) switch place at 90°. Likewise, the HOMO–1 interchange with the HOMO–2, and the LUMO+1 with the LUMO+2. From the perspective of orbital helicity, the LUMO eigenvalue is lowered by the torsion as the orbital-helix is being unwound; the HOMO eigenvalue rises as the orbital-helix is being overwound by the axial torsion. The molecule formally becomes a diradical at 90° and we note that a multi-reference computational approach must be used to fully

assess the transport and electronic properties of this transition state, rather than the singlet ground-state approach we apply here;<sup>99</sup> see SI part A for a brief comparison of methods.



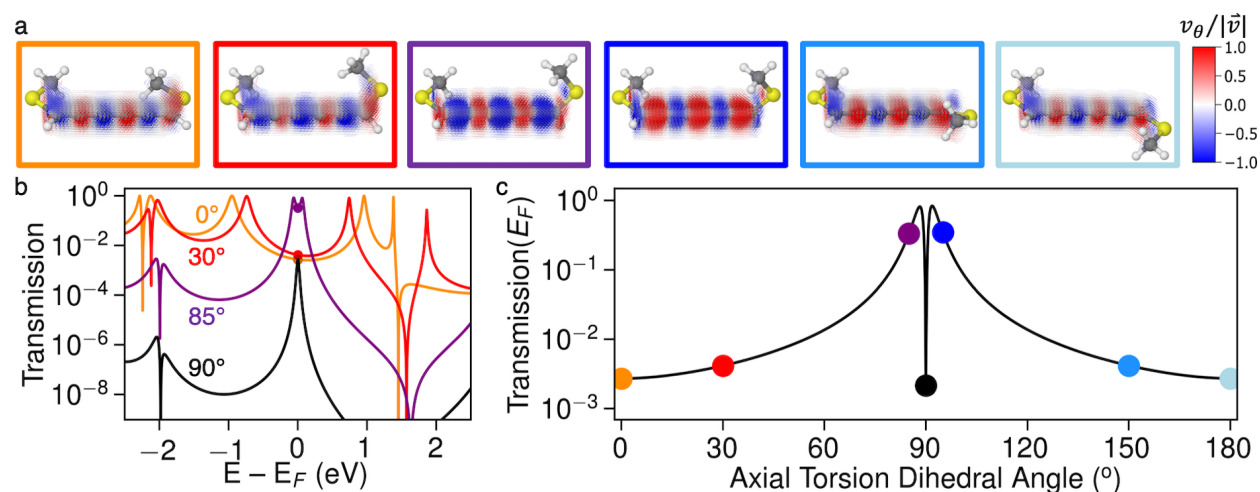
**Figure 6.** Change of the frontier molecular orbitals of **[5]cumulene-SMe** under axial torsion. a) Eigenvalues of the frontier molecular orbitals plotted as a function of dihedral angle. b) Iso-plot of the four frontier molecular orbitals at dihedrals angles of 0°, 30°, 85°, 95°, 150°, and 180°, the molecular structures are shown at the top, followed by the LUMO+1, LUMO, HOMO, and HOMO-1 at the bottom.

**ELECTRON TRANSPORT.** Shown in Figure 7, the ballistic current density and electronic transmission is calculated for **[5]cumulene-SMe** under axial torsion. With co-planar end-groups at 0° and 180° torsion, the current follows a largely linear path through the  $\pi$ -system (current density arrows are almost white due to the small  $\theta$  vector-component, see also Figure S21 and S24). As in the case of **triyne-SMe** at 0° and 180° torsion (Figure 5), there are weak ring currents centered at the carbon atoms alternating in direction with every atom. These ring currents become increasingly clear around the wire when axial torsion is applied as seen by the change of color towards stronger blue and red colors (clockwise and counter-clockwise directions). At 85° and 95° torsion, strong ring currents are centered around the bonds of the carbon wire, now alternating in

direction with every cumulenic bond. The ring current pattern reverses at  $90^\circ$ , again in correlation with the HOMO and LUMO helicity interchanging (see Figure 6).

The transmission profile of odd- $n$  cumulenes is quite distinct from that of the polyynes. Shown in Figure 7c for **[5]cumulene-SMe**, under axial torsion from the two ground-state structures at  $0^\circ/180^\circ$  the transmission at the Fermi energy rises almost until  $90^\circ$  torsion. Despite that the end-groups are almost perpendicular at  $85^\circ/95^\circ$  torsion the transmission is very high. The increase of transmission with torsion is a consequence of the decreasing HOMO-LUMO gap and will be accompanied by an increase in the diradical character of the molecule.<sup>54, 100</sup> As the HOMO-LUMO gap vanishes, electron transport under bias will eventually change from off-resonant to resonant tunneling, although only few molecular systems have been reported which achieve resonant transport without a gate-electrode.<sup>101-102</sup>

At  $90^\circ$  there is a steep drop of the transmission because the HOMO and LUMO become degenerate. As with the **triyne-SMe** at  $90^\circ$  torsion, the orbital symmetries means that the transmission is suppressed when frontier molecular orbitals become degenerate due to destructive quantum interference.<sup>94-98</sup> The relation to destructive quantum interference is also evident by the fact that the directions of the ring currents revert at  $90^\circ$  torsion.<sup>56</sup> The full transmission plots at  $95^\circ$ ,  $150^\circ$  and  $180^\circ$  are almost identical to those at  $85^\circ$ ,  $30^\circ$ , and  $0^\circ$  and are shown in Figure S4.



**Figure 7.** Current density and transmission of [5]cumulene-SMe under axial torsion. A) Current density calculated at the Fermi energy colored by the normalized  $\theta$  vector component at dihedral angles (from left to right)  $0^\circ$ ,  $30^\circ$ ,  $85^\circ$ ,  $95^\circ$ ,  $150^\circ$ , and  $180^\circ$ . The current density vector field is plotted as arrows that are normalized in each plot; each arrow is colored by its circular vector component ( $v_\theta$ ) normalized relative to its total vector length. High resolution images are included in SI part H. b) Transmission plotted semilogarithmically against energy at select dihedral angles. c) Transmission at the fermi energy plotted against the torsion dihedral angle.

## EVEN- $n$ CUMULENIC CARBON WIRES

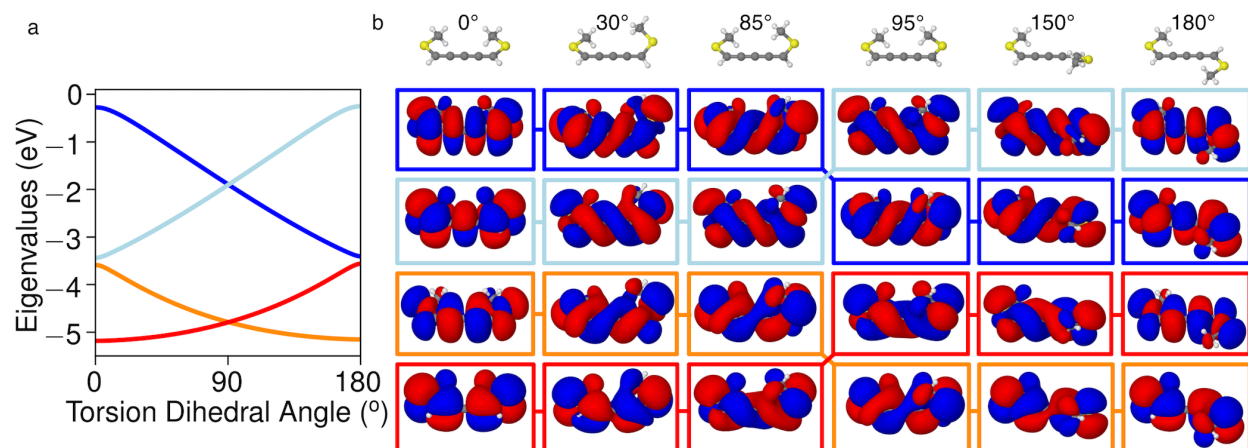
Even- $n$  cumulenes have many of the same structural traits as the odd- $n$  cumulenenic systems with almost no bond-length alternation, lower stability than polyynes, and considerable axial torsion barriers (see Figure 3). Unlike the other two types of linear carbon wires, even- $n$  cumulenes have an odd number of carbon atoms in the linear chain and achieve closed-shell electronic structure by having perpendicular end-groups. Owing to the orientation of the end-groups, there is not much electronic communication through the  $\pi$ -systems of molecule; the single-molecule conductance of

a functionalized [2]cumulene (allene) was recently measured to be almost two orders of magnitude lower than that of the equivalent [3]cumulene.<sup>19</sup> However, we recently demonstrated that the electronic transmission through even-*n* cumulenes can be almost as high as that of the equivalent odd-*n* systems by splitting the helical frontier molecular orbitals using pyramidalized  $\pi$ -donor substituents. Strategies for manipulating the helical electronic structure of cumulenes using substituents is described in detail elsewhere.<sup>39-40, 45-46</sup>

**ELECTRONIC STRUCTURE.** The four frontier molecular orbitals and their eigenvalues are calculated for the **[4]cumulene-SMe** in Figure 8. In the ground-state structure at approximately 90°, each of the helical orbital pairs (HOMO-1 and HOMO, LUMO and LUMO+1) are near-degenerate. Depending on the torsion away from 90° the orbital pairs split in each direction and the HOMO-LUMO gap narrows. As in the previous two cases, the molecular orbitals have a clear helical shape when the end-groups are in a non-planar geometry (including that at 90°) because a helicogenic symmetry is achieved.<sup>39, 43</sup>

The orbital helicity of the HOMO and LUMO will vary as different helical orbitals are (de)stabilized depending on the direction of the axial torsion from the ground-state structure at 90°. This is seen in Figure 8, for example by comparing the helicities of the HOMO at 30° and 150°, in the first case a minus helix and in the second case a plus helix. We can trace the gradual evolution of the molecular orbitals from 90° towards 0° in Figure 8. As torsion is applied from 85° to 30°, the HOMO (orange in Figure 8) is destabilized as it is a helix that is being overwound, and the LUMO (light-blue in Figure 8) is stabilized as it is a helix that is being unwound. Thus, the HOMO-LUMO gap narrows and almost vanishes at 0°. At 0° and 180°, the two  $\pi$  orbital systems are separated by symmetry because the end-groups are co-planar, and finally take the normal rectilinear shape.





**Figure 8.** Change of the frontier molecular orbitals of **[4]cumulene-SMe** under axial torsion. a) Eigenvalues of the frontier molecular orbitals plotted as a function of dihedral angle. b) Iso-plot of the four frontier molecular orbitals at dihedral angles of 0°, 30°, 85°, 95°, 150°, and 180°, the molecular structures are shown at the top, followed by the LUMO+1, LUMO, HOMO, and HOMO-1 at the bottom.

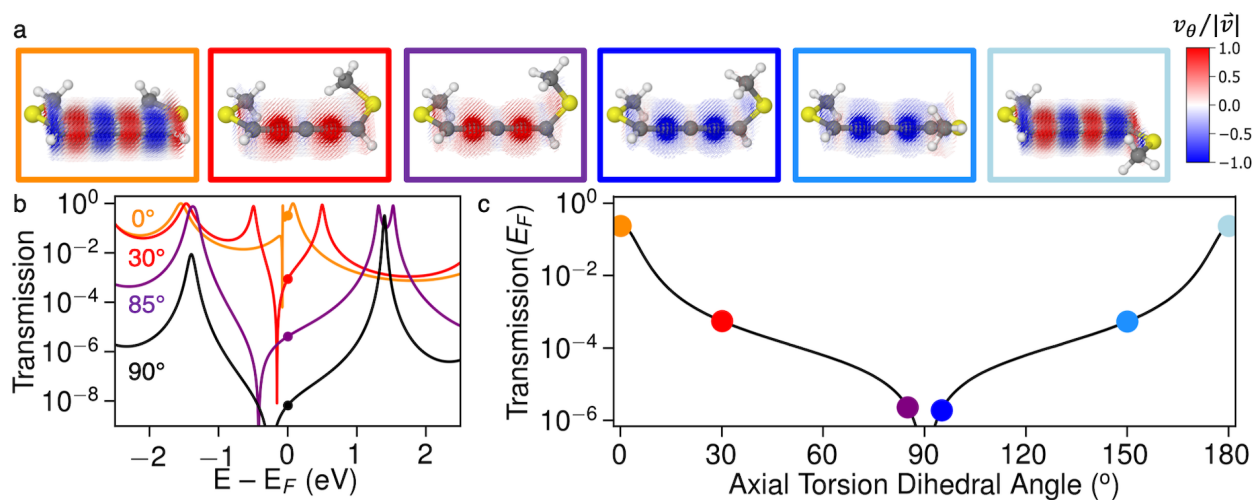
ELECTRON TRANSPORT. Shown in Figure 9, the ballistic current density and electronic transmission is calculated for **[4]cumulene-SMe** under axial torsion. Strong ring currents are present around the wire near the ground-state structure with perpendicular end-groups (current density arrows are blue or red due to the large  $\theta$  vector-component, see also Figure S26 and S27). Depending on the direction of torsion from 90° the ring currents have opposite directions, again in direct correlation with the change of orbital helicity at 90° (see Figure 8). Consequently, the ring currents are counter-clockwise around the wire at 85° torsion angle and clockwise around the wire at 95° torsion angle (arrows are red/blue due to positive/negative  $\theta$  vector component). Different from **[5]cumulene-SMe** and **triyne-SMe** where the ring currents are centered around bonds, the ring currents of **[4]cumulene-SMe** are centered around the atoms. The ring currents around the

wire persist even as the torsion angles approach  $0^\circ/180^\circ$ . With co-planar end-groups the direction of the ring current alternates with the ring currents centered around the wire are centered around the bonds rather than the atoms; these ring current remain although there is no clear helicity in the frontier orbitals of these configurations of the molecule (see Figure 8). By inspection, the current density appears more turbulent in the co-planar configurations, see Figure S25-S28 in Supporting Information.

From the transmissions plotted in Figure 9b, it is clear that the transmission at all torsion angles is dominated by a sharp antiresonance near the Fermi energy. Despite breaking the near-degeneracy of the frontier orbitals at  $90^\circ$  torsion, this suppression of the transmission remains within the HOMO-LUMO gap. The energy of the antiresonance is subject to the Fermi energy alignment which cannot reliably be determined using density functional theory (DFT); we return to this issue in the discussion section. As we use s-band electrodes in the calculations presented here, the Fermi energy is almost unchanged with torsion. Therefore we see in Figure 9b that as the HOMO-LUMO gap narrows when the torsion angle approaches  $0^\circ/180^\circ$ , the transmission at the Fermi energy rises. As seen in other  $\pi$ -conjugated molecules, strong ring currents often appear when there are antiresonances in the transmission.<sup>56</sup> However, the total current is also very low in such cases as the transmission is suppressed. It is visually clear that the circular currents are stronger than the net current through the molecules. As the torsion angles approach  $0^\circ/180^\circ$  the total current becomes higher and the current density pattern alternates in terms of its circular direction.

The transmission profile of even- $n$  cumulenes under torsion is different from both polyynes and odd- $n$  cumulenes. This clearly reveals the need to consider even- $n$  and odd- $n$  cumulenes as separate classes of carbon wires until the true polymeric limit of carbyne is reached. Shown in Figure 9c

for **[4]cumulene-SMe** under axial torsion from the ground-state structure at  $90^\circ$ , the transmission at the Fermi energy initially follows a  $\cos^2$ -dependence like polyynes and biphenyls. However, as the molecule approach a structure with co-planar end-groups the HOMO-LUMO gap narrows and the transmission becomes higher than in polyynes and odd- $n$  cumulenes with equivalent torsion angles. Unlike **triyne-SMe** and **[5]cumulene-SMe** which we examined in the previous two sections, the trend shown in Figure 9c for **[5]cumulene-SMe** is subject to the Fermi energy alignment due to the antiresonance in the transmission. However, we shall see in the next section that the predicted trend in the transmission is a general feature of even- $n$  cumulenic wires.



**Figure 9.** Current density and transmission of **[4]cumulene-SMe** under axial torsion. A) Current density calculated at the Fermi energy colored by the normalized  $\theta$  vector component at dihedral angles (from left to right)  $0^\circ$ ,  $30^\circ$ ,  $85^\circ$ ,  $95^\circ$ ,  $150^\circ$ , and  $180^\circ$ . The current density vector field is plotted as arrows that are normalized in each plot; each arrow is colored by its circular vector component ( $v_\theta$ ) normalized relative to its total vector length. High resolution images are included in SI part H. b) Transmission plotted semilogarithmically against energy at select dihedral angles. c) Transmission at the fermi energy plotted against the torsion dihedral angle.

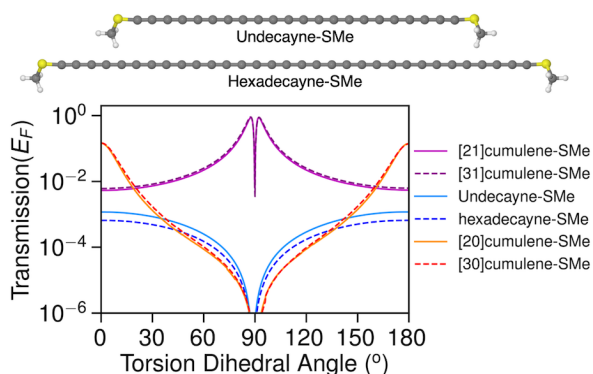
## DISCUSSION

In the three results sections we have shown that three distinct transmission profiles exist for **triyne-SMe**, **[5]cumulene-SMe**, and **[4]cumulene-SMe**. We expect these trends to be largely independent of functional groups as all closed-shell carbon wires are expected to fall within the three types of linear carbon wires (in the limit that they can be considered molecules); two examples are included in SI part C.

In our computational studies of **triyne-SMe**, **[5]cumulene-SMe**, and **[4]cumulene-SMe** we strictly deal with the singlet ground-state as determined using DFT. It is clear that this approach may not be sufficient in systems with high diradical character,<sup>99</sup> such as **[5]cumulene-SMe** in configurations approaching 90° and **[4]cumulene-SMe** approaching 0°. Tests using complete active space self-consistent field (CASSCF) presented in SI part A suggest the discrepancy may be qualitative, although we are not able to verify this with transport calculations at the same level of theory. In potential transport experiments where a substantial bias is applied, the diradical character is likely to become zwitterionic character due to the electric field.<sup>20</sup> Further work must be done to fully understand such cases where the ground-state HOMO-LUMO gap vanishes.

**LENGTH DEPENDENCE.** The wires we examined here are short molecules. It is clear that the trends will break down at some length. When the polymeric limit of true carbyne is reached, its properties will be those of the polyyne or the cumulenene structure because the odd- $n$  and even- $n$  of cumulenes is an edge effect. Furthermore, coherent off-resonant transport is not likely to be the dominant charge transport mechanism in very long molecular wires where structural fluctuations and distortions may distort the effect of torsion. From a purely theoretical perspective, we expect the trends to be qualitatively independent of molecular length because all three types of wires are isolobal with alternant molecular systems,<sup>39, 103-104</sup> and the change of the electronic structure with

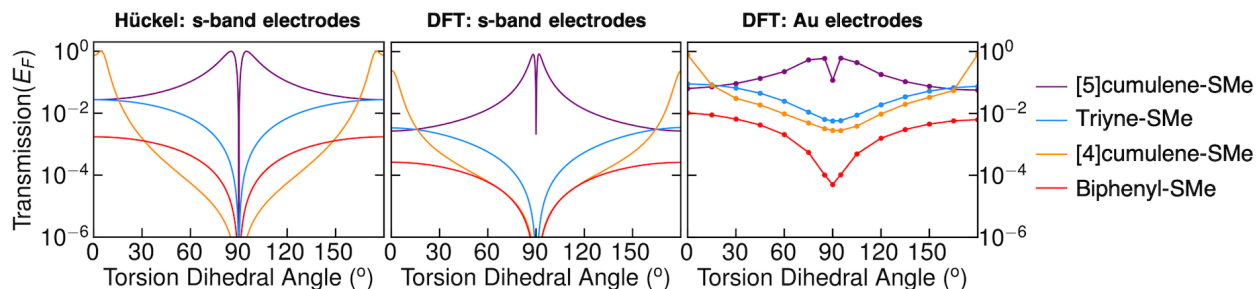
length is systematic in finite molecular systems.<sup>69, 105</sup> To a certain extent this can be verified with calculations on finite-length molecules. In Figure 10, we show the transmission profile under axial torsion for the three types of linear carbon wires with lengths of 21, 22, 31, and 32 atoms. The plots are very similar to those for the short wires we explored in the previous sections, and barely change when going from 22 (21) to 32 (31) atoms in the wire. At the scale of length where these transmission profiles may change coherent off-resonant transport is unlikely to be effective. Within the limit of coherent transport, axial torsion may serve as a test for whether a wire is in the molecular regime with three different structure types, or if the wire has reached the polymeric limit of carbyne where there are only two structure types.



**Figure 10.** Top) Optimized molecular structures of thiomethyl-functionalized **undecayne-SMe** (22 carbon polyyne) and **hexadecayne-SMe** (32 carbon polyyne). Bottom) Transmission at the Fermi energy plotted against the axial torsion dihedral angle for long thiomethyl-functionalized cumulenic and polyyenic molecular wires.

**JUNCTION MODELS.** In the three results sections we calculated the transmission with wide-band approximated s-band electrodes using DFT. This approach has the advantage of not being electrode-specific (what we calculate are properties of the molecule) and the electronic structure is calculated at a reasonable level of theory. Still, we think it is worthwhile to consider the generality of our approach. In Figure 11, we have furthermore carried out the transmission

calculations using Hückel theory with s-band electrodes and DFT with Au-electrodes (we refer to the method section for computational details), the full transmission plots are included in SI part D. The transmission profiles with torsion are very similar with these three types of calculations. Using Hückel theory the electronic structure is idealized and consequently perfect suppression is achieved at  $90^\circ$  in all systems. Using DFT with Au-electrodes electronic degeneracies are broken and full suppression is never achieved; bulky Au electrodes may furthermore have higher coupling into the  $\sigma$ -systems of the molecules. It is clear that the trend of the transmission with axial torsion is very consistent from the most simplified level of theory to DFT calculations where the metal electrodes are fully considered. These trends are to be observed in single-molecule junction experiments if suitable ways of controlling the axial torsion can be realized, for example by constrained molecular designs or rotatable electrodes.



**Figure 11.** Transmission at the Fermi energy plotted against the axial torsion dihedral angle using three different calculation setups. Left) Using a simple Hückel model. Note that for [4]cumulene  $E_F = -0.1$  eV. Middle) Using DFT with wide-band approximated s-band electrodes. Right) Using DFT with periodic Au electrodes.

We note that the Hückel calculations (SI part F) provide further insight into the suppression of the transmission in even- $n$  cumulenes due to destructive quantum interference. At this level of theory, the antiresonance in the transmission of **[4]cumulene-SMe** is exactly in the middle of the HOMO-LUMO gap (the Fermi energy), and while the HOMO-LUMO gap narrows as the torsion

angles approaches  $0^\circ/180^\circ$  the antiresonance does not change energy (see Figure S7). Therefore, we plot the transmission at  $E_F = -0.1$  eV for **[4]cumulene-SMe** in Figure 11. However, this also shows that the antiresonance is not affected by the torsion and given it is unusual that the antiresonance is exactly at the Fermi energy in a realistic setup, we find that the trends presented in Figure 11 are more likely to be observed in an actual experiment.

## CONCLUSIONS

In this work we have traced the change of electronic structure, ballistic current density, and Landauer transmission of linear carbon wires during axial torsion. All types of cumulenic and polyynic carbon wires exhibit helical  $\pi$ -orbitals when the end-groups are not in co-planar orientation. This helical electronic structure gives rise to ring current patterns around the linear wires, and for all three classes of wires we see a correlation between the change of frontier orbital helicities and the direction of the ring currents around the wire. It is hard not to speculate that ring current patterns around the axis of linear molecular wires can provide novel functionality in carbyne-based molecular electronics components. For example, it has been suggested that helical currents around an axis can induce a unidirectional rotation in the molecule due to the conservation of the total angular momentum,<sup>106-107</sup> thus making the linear segment of the molecule function as a current-driven motor. The circular movement of charge will also generate a local unidirectional magnetic field in the molecule,<sup>108-109</sup> which may allow for magnetic control of the single-molecule conductance,<sup>110-114</sup> a direction we are working towards exploring. Realizing the potential of helical currents in truly linear molecules poses an interesting challenge for the field of molecular electronics.

We have demonstrated that polyynes, odd- $n$  cumulenes, and even- $n$  cumulenes exhibit distinctively different transmission profiles under axial torsion. Most notably, we predict that the transmission of odd- $n$  cumulenes rise with torsion from  $0^\circ/180^\circ$  towards  $90^\circ$  dihedral angle. The well-known cos-squared dependence of the transmission with axial torsion is a special case, which in the case of linear carbon wires only holds for even-carbon polyynic systems. The finding of three distinctive transmission profiles with torsion suggest that odd- $n$  and even- $n$  cumulenes are to be considered as separate types of carbyne-like molecules. Along with polyynes, odd- $n$  and even- $n$  cumulenes form the three classes of closed-shell carbon wires in the molecular limit. The identification of three regimes of axial torsion may allow for the identification of the polyynic or cumulenic nature of experimentally accessible carbyne wires.

## METHODS

In this work we explored the electronic structures and electron transport properties of linear carbon molecules under axial torsion. The molecular structures were optimized to the *verytight* criteria using DFT with the Perdew-Burke-Ernzerhof (PBE) functional and 6-311G(d,p) basis set as implemented in Gaussian09.<sup>115-116</sup> The dihedral angles were manipulated directly on the optimized structure of each molecule without further optimization. Specifically, these were the Me-S—S-Me dihedral angle for **triyne-SMe** (long line indicating that the two atoms are not nearest neighbors), the S-C—C-S dihedral angles for **[4]cumulene-SMe** and **[5]cumulene-SMe**, and one of the C-C-C-C dihedral angles (connecting the two rings) for **biphenyl-SMe**.

The electronic structure calculations presented in the manuscript were carried out using DFT as implemented in Atomic Simulation Environment (ASE) and GPAW.<sup>117-118</sup> We used the PBE



functional with double- $\zeta$  plus polarization (DZP) basis set for all atoms.<sup>119</sup> This level of theory was chosen in order to carry out the transport calculations. Based on the torsion energy profiles (Figure 3) which we have also calculated at the M06-2X(D3) level of theory as implemented in Gaussian09 and CASSCF as implemented in Dalton (Figure S1),<sup>116, 120-122</sup> we expect results to be qualitative similar at higher levels of theory. All molecular structures, orbitals, and current density plots were made using Jmol.<sup>123</sup> Molecular orbitals were plotted using the default isosurface value of 0.02.

Electron transport calculations were carried out using the non-equilibrium Green's functions (NEGF) approach in combination with DFT as implemented in ASE and GPAW,<sup>117-118</sup> or with a Hückel model where noted. The retarded and advanced Green's functions,  $G^{r/a}(E)$ , are calculated from the Hamiltonian and overlap matrix of the molecular region,  $H_M$  and  $S_M$ , and the self-energies of the left and right electrodes,  $\Sigma_{L/R}^{r/a}(E)$ ,

$$G^{r/a}(E) = [E \cdot S_M - H_M - \Sigma_L^{r/a}(E) - \Sigma_R^{r/a}(E)]^{-1}. \quad (1)$$

The Landauer transmission,  $T(E)$ , is then calculated using the coupling matrices of the left and right electrodes,  $\Gamma_{L/R}$ ,

$$T(E) = \text{tr}[\Gamma_L(E)G^r(E)\Gamma_R(E)G^a(E)]. \quad (2)$$

Except where otherwise noted, electron transport and current density calculations presented in the manuscript are modelled using single-molecule junctions with s-band electrodes. These junctions were formed using two dihydrogen molecules placed with an S-H distance of 1.75 Å, a C-S-H bond angle of 110°, and C-C-S-H dihedral angle of 120° (for **triyne-SMe** this is defined by the methyl group), thus forming the extended molecular region used in equation 1. The s-band electrodes were formed using the wide-band approximation with nonzero matrix elements of  $\Gamma_{L/R}$  set to  $\gamma = 1.0$  eV. This approach gives a qualitatively similar transmission to using periodic Au-electrodes, and allows us to calculate the ballistic current density.<sup>55, 84</sup> Both transmission and

current density calculations were carried out using DFT with the PBE functional and DZP basis set for all atoms except hydrogen where a SZ basis was used. A Fermi temperature is applied to ensure convergence for systems with vanishing HOMO-LUMO gap, which corresponds to a width of 0.1 in the Fermi function. We carried out these calculations using our homemade transport and current density code which is compatible with GPAW and ASE,<sup>117-118</sup> and freely available at [https://github.com/marchgarner/Current\\_Density.git](https://github.com/marchgarner/Current_Density.git); a brief description of the approach follows here.

At zero-temperature and absent of an external magnetic field, using the NEGF formalism the low-bias current density  $\mathbf{j}(\mathbf{r})$  was calculated by equation 3, where  $\psi$  are basis functions, and  $C$  are the functions within the extended molecular region which we sum over.<sup>124-125</sup>

$$\mathbf{j}(\mathbf{r}) = \frac{ie^2\hbar}{4m\pi} \sum_{i,j \in C} \int_{-\infty}^{\infty} dE G_{ij}^n [\psi_i(\mathbf{r})\nabla\psi_j(\mathbf{r}) - \psi_j(\mathbf{r})\nabla\psi_i(\mathbf{r})] \quad (3)$$

$$G^n = iG^r\Gamma_L G^a\delta V \quad (4)$$

Here,  $G^n$  is the non-equilibrium part of the lesser Green's function and  $\delta V$  is a small symmetric bias difference between the electrodes, which we set to  $\delta V = 1$  mV. Each vector in the vector field is plotted as an arrow of same length; the vector-length (the magnitude of the current density at position  $\mathbf{r}$ ) is the radius of the arrow and is scaled relative to the largest arrow in the same figure. Vectors smaller than 5% of the largest z-component are not included for clarity, z being the transport direction. We calculated the current density in a cylindrical coordinate system, which allow us to color the arrows by the relative cylindrical vector-component  $\frac{v_\theta}{|\vec{v}|}$ . The conversion from cartesian to cylindrical coordinates is trivial, and is included for reference in SI part H. Finally, as we and other have recently noted,<sup>45, 55, 126-129</sup> ballistic current density calculations can have serious issues with current conservation over the molecule due to using a finite local basis set and approximated core-potentials; we provide some examples of this problem in SI part G.

As described in the Discussion section, we also carried out transport calculations using two alternative calculation setups. For the most simplistic approach to coherent electron transport, we produced Hückel models for each molecule, which is described in detail in SI part F. For more realistic modelling of Au-molecule-Au junctions, we carry out the calculations using DFT as implemented in ASE and GPAW with the PBE functional and DZP basis set for all atoms.<sup>115, 117-</sup>  
<sup>119</sup> The junction structure is formed by placing the molecular structure between two 4-atom Au pyramids on  $4 \times 4$  Au(111) surfaces with periodic boundary conditions in the plane of the surfaces. From this junction structure the Landauer transmission is calculated using equation 2 with a k-point sampling over a  $4 \times 4 \times 1$  Monkhorst–Pack mesh in the first Brillouin zone.

**Supporting Information.** Level of Theory. Electronic Structure of Biphenyl. Alternative End-groups. Transmission Plots. Transmission with Gold Electrodes. Hückel Models. Convergence of Current Density. High Resolution Images of Current Density.

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