Fused Helicenes

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Alkynes as Linchpins for the Additive Annulation of Biphenyls: Convergent Construction of Functionalized Fused Helicenes

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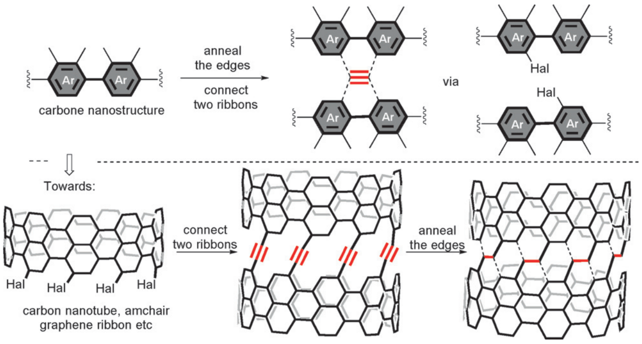
Abstract: *A new approach to fused helicenes is reported, where varied substituents are readily incorporated in the extended aromatic frame. From the alkynyl precursor, the final helical compounds are obtained under mild conditions in a two-step process, in which the final C−C bond is formed via a photochemical cyclization/ dehydroiodination sequence. The distortion of the π-system from planarity leads to unusual packing in the solid state. Computational analysis reveals that substituent incorporation perturbs geometries and electronic structures of these nonplanar aromatics.*

The armchair edge is a common structural feature of carbon-rich nanostructures (nanotubes, graphene ribbons etc). Scott described a creative Diels–Alder strategy for the growth of such nanostructures from the "biphenyl-like" bay regions.[1] Although this approach is hampered by the weak reactivity of acetylene, more reactive analogues such as nitroethylene can be used, albeit still at relatively harsh conditions.[1,2] Intrigued by the recent report of selective edge halogenation procedures for nanographenes[3] that may allow alkyne introduction at these positions, we became interested in testing the possibility of using alkynes as a two-carbon unit for connecting two armchair-edged carbon nanostructures (Scheme 1). The basic step of such process is the annulation of two biphenyl units. This work reports a simple method for such transformation for the model system and illustrates the utility of this approach for the preparation of distorted helicene aromatics.



Scheme 1. Proposed use of alkynes for annealing two biphenyl systems and its possible implications for chemistry of carbon nanostructures.

Curvature introduces a new design element for controlling the organization of aromatics into 3D crystal architecture.[4] By using a nonplanar core, the aromatic rings may adopt unusual intermolecular interaction patterns that are typically unavailable to flat molecules. In helicenes, distortion from a planar topology is induced due to *ortho*-annelation of the polycyclic aromatic framework. Owing to unique spectral, optical, and structural properties,[5] helicenes are investigated for application in nanoscience,[6] asymmetric catalysis,[7] chemical biology, supramolecular, and polymer chemistry.[8]

Synthetic methods that allow facile control over size, rigidity, thermal stability, and functionality are crucial for advancing the utility of helicenes.[9,10] Recent reports,[11,12] have leveraged the propensity of alkynyl precursors to form carbon rich conjugated structures.[13] Despite significant progress in the area, the list of general methods that can produce a large library of helicenes with a broad selection of precisely placed functional groups is still limited.[14]

An attractive metal-free approach to additive annulation of biphenyls would be to couple iodo-cyclization of alkynes with directed Mallory photocyclization of the *o*-terphenyl intermediate.[15,16] The advantage of this approach is that the dearomatized dihydrophenanthrene intermediates derived from the iodo-substituted substrates can undergo irreversible rearomatization via simple elimination of HX under mild conditions. The use of such "preoxidized" substrates with an electronegative substituent, X, on one of the reacting carbons at the ring closure point obviates the need for an external oxidant for the aromatization step. Most of the effort has focused on $X = Cl$,[17] Br,[18] OMe[19] and more recently $X = F$[20] while surprisingly little is known about iodinated *o*-terphenyls.[21]

Undeterred by this scarcity, we decided to explore the possibility of coupling iodocyclizations[22] to light-induced cyclodehydroiodination (CDHI). Aryl iodides can be conveniently prepared from alkynes in iodocyclization processes that give the bonus of annealing an additional cycle with the properly positioned iodo group. In this scenario, the introduction of iodine is transient (it can be considered a traceless directing group if the two cyclization steps are taken together). In the overall cascade, the alkyne moiety serves as a staple that "stiches" the two biphenyl systems together. A similar approach was used by Liu and co-workers[23] but the last step was a Pd-catalyzed Mizoroki–Heck coupling. In this work, we report an equally efficient photochemical proce-

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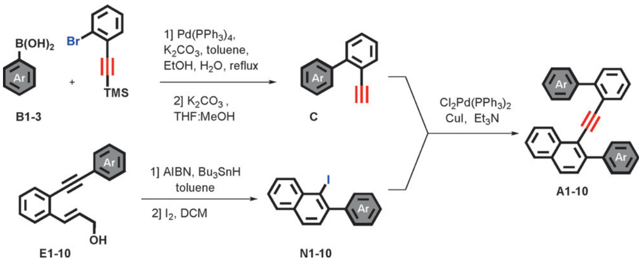
dure, which offers the practical advantage of avoiding the use of a transition metal catalyst.

The starting point for our approach was the synthesis of a diverse library of α-iodo-β-substituted naphthalene building blocks **N1–10**. For this purpose, we took advantage of our Bu_3SnH-mediated radical cyclization/fragmentation cascades of *ortho*-enynes,[24] followed by in situ quantitative iododestannylation, with I_2 in DCM, which provided **N1–10**, as shown in Scheme 2.



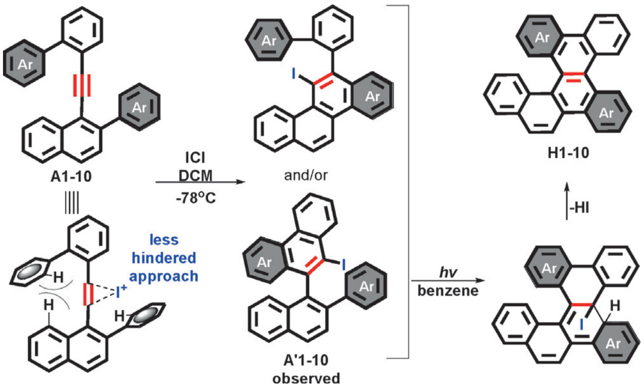
Scheme 2. The synthetic route for preparing the alkynyl precursors of helicenes **A1–A10**.

The second set of required structural units (2-ethynylbiphenyls) was assembled via Suzuki cross coupling of *o*-bromophenyl TMS alkynes with different boronic acids, **B1–B3** followed by desilylation with K_2CO_3 in 1:1 THF:MeOH. Subsequent Sonogashira cross coupling of the α-iodo, β-substituted naphthalenes[23] and the ethynyl biphenyl derivatives **C** yielded a library of the key bis(biaryl) acetylene precursors **A1–A10**.[25] To expand the general applicability of the protocol for the synthesis of 5,5 fused carbohelicenes such as helicene **H10**, we ran the Sonogashira cross coupling with 1-iodo-2,2′-binaphthalene and 2-ethynyl-1,1′-biphenyl and obtained the internal alkyne precursor **A10** in good yield of 86 %.

The first core ring of the helicene frame is assembled by treating each bis(biaryl)acetylene **A1–A10** with 1.1 equiv of ICl in DCM at −78 °C for 2–3 hours. The iodonium-induced carbocyclization could afford either the substituted iodochrysene, iodophenanthrene, or a mixture of both. The convenience of this convergent synthetic strategy is that the subsequent photochemical CDHI step should convert either structural isomer into the same final helical products, **H1–H10**, as shown in Scheme 3.

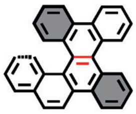
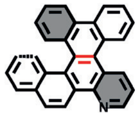
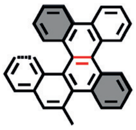
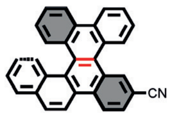
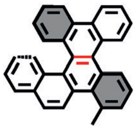
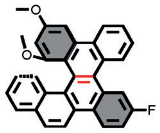
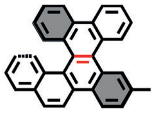
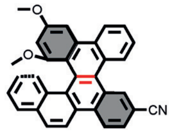
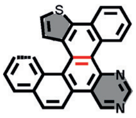
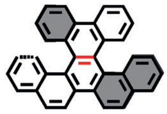
Interestingly, we observed selective carbocyclization into the iodophenanthrene derivatives. The observed regioselectivity is likely due to less steric congestion upon coordination of I^+ to the alkyne away from the naphthyl moiety.

Photochemical closure of iodophenanthrene derivatives **A′1–10**, driven by the release of HI, readily afforded the functionalized fused helicenes shown in Table 1. This process allows access to structurally diverse substrates containing functional groups such as Ph (**H1**), tolyl derivatives (**H2–H4**), methoxy and dimethoxy aryls (**H8–H9**), as well as heterocyclic thiophene and pyridine units placed at the termini of the helicene scaffold (**H5–H6**). However, photocyclization of the aryl iodide produced from pyridyl acetylene **A6** was inefficient, yielding helicene **H6** in 35 % yield.[26]



Scheme 3. ICl cyclization does not have to be selective when coupled with convergent photochemical CDHI.

Table 1: The library of fused helicenes **H1–H10**.

Helicene		Yield	Helicene		Yield
H1		82 %	**H6**		35 %
H2		89 %	**H7**		93 %
H3		91 %	**H8**		81 %
H4		91 %	**H9**		90 %
H5		90 %	**H10**		80 %

The methodology can be readily extended to the higher homologues such as [5,5]helicene **H10**. ICl-induced carbocyclization onto the alkyne provided the iodinated compound in almost quantitative yield. Photochemical closure was successful in affording the [5,5] helicene **H10** in 80 % yield. In general, we found that the addition of propylene oxide (excess) was helpful to the reaction, likely assisting as an acid scavenger of in situ generated HI. One notable benefit of this directed photochemical CDHI process is that the lack of external oxidant prevents further cyclization of the newly formed helicenes.[27]

The helical structures of **H2** and **H7** were unambiguously determined by X-ray crystallographic analysis (Figure 1), which confirmed an extended doubly twisted π-system for both structures. The compounds crystallize in the space groups *P*21/*c* and *Pbca*, respectively. For both structures, significant bond length alternation originates from deviation

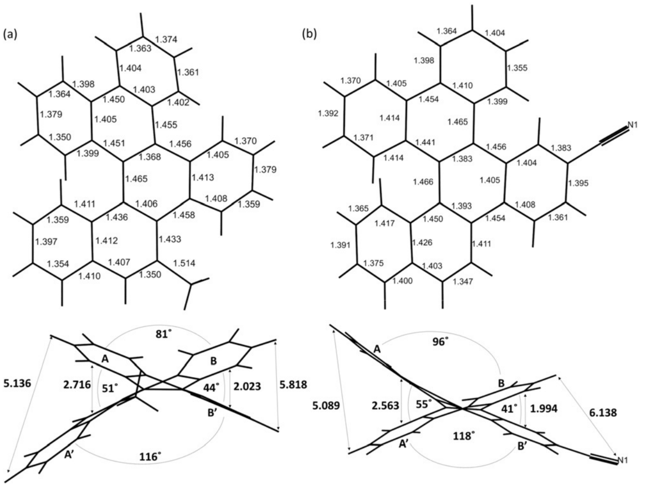


Figure 1. Crystal structures of a) [4,5]-fused helicenes **H2** and b) **H7**, with the bond lengths shown in Å.

from planarity and from differences in the aromatic character, particularly in the central naphthalene subunit. The bond lengths, the dihedral angles between the planes of the terminal rings, A–A′ and B–B′, and the distances of the inner and outer helical pitch between rings A and A′ and rings B and B′ are shown in Figure 1.

The presence of different substituents in the helical skeleton leads to substantial differences in the crystal packings of **H2** and **H7**. In both crystal structures, the molecules form π-π stacks along the b axis or the a axis of the lattice, respectively. In the crystal structure of **H2** which contains columns of molecules with the same handedness, the stacks are held together by effective π–π interactions between rings A ($d_{\text{ring-ring}} = 3.40$ and 3.52 Å), which result in the CH_3 substituents of one stack facing the CH_3 substituents of the neighboring stack (Figure 2a). Such arrangement leads to alternating π-π-interdigitated and CH_3-lined regions. The CH_3 groups are engaged in σ–π interactions with the inner ring of the neighboring molecule, with the H-centroid distance of 2.59 Å (Figure 2b). The entire crystal packing thus exhibits extensive intermolecular π–π and σ–π contacts that minimize the free space between the stacks (Figure 2c). Note that extensive π–π contacts exist both inside the columnar stacks and between them.

The crystal packing of **H7** is markedly different. It is dominated by intermolecular π–π contacts between the curved π-surfaces within the same stack while interactions between the stacks are provided by σ-π- contacts (Figure 3a). Thus, the interdigitation between the stacks is minimal, which leads to the crystal packing with quite large open channels. These openings are filled with strongly disordered hexane molecules (Figure 3b) The crystal packing in this compound can be considered reminiscent of metal–organic or covalent–organic frameworks,[28] but in the present case the molecules are held together via the combination of shape complementarity and weak supramolecular interactions to create the open-pore structure.

Interestingly, unlike the CH_3-substituted derivative **H2**, in which each methyl group shows preferred interaction with the inner ring of the neighboring molecule, in the structure of **H7**, the cyano group positions its terminal N atom over the outer A′ ring, with the N–centroid distance of 3.740 Å. Thus, the variation of the substituent offers a viable approach to achieving specific crystal packing effects.

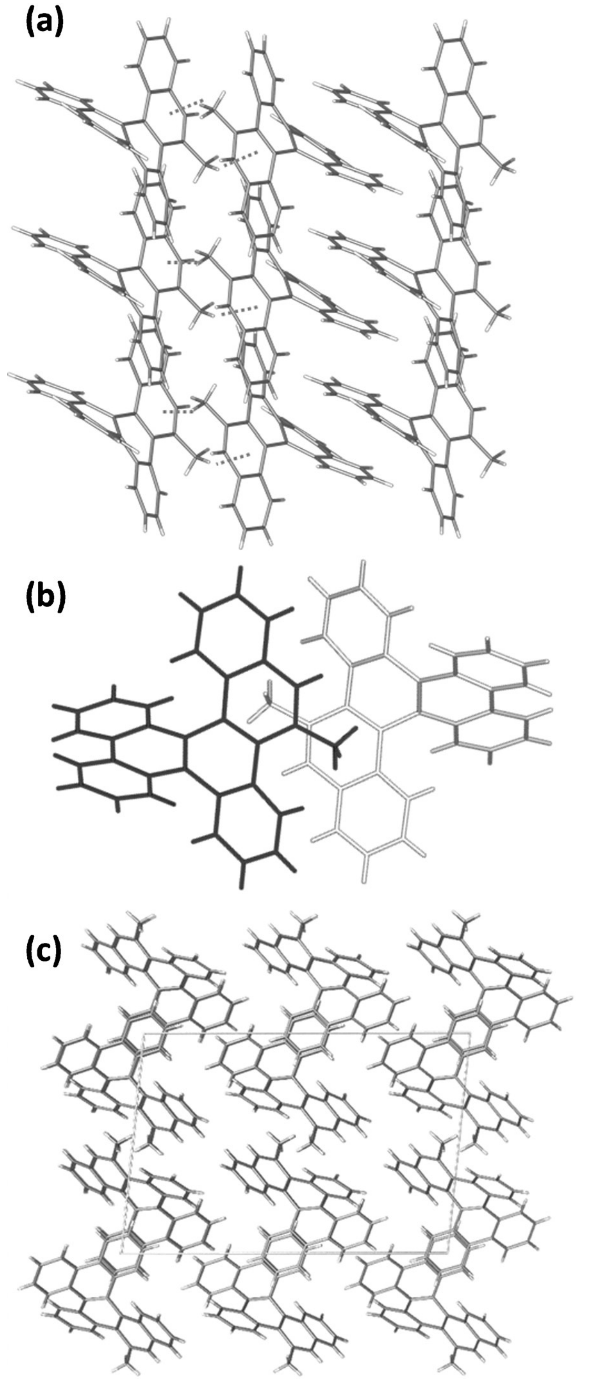


Figure 2. Crystal packing of **H2**: a) a side view of stacks revealing regions dominated by π–π and σ–π (dashed lines) interactions; b) the σ–π interaction between the methyl groups and the inner rings of the molecules; c) crystal packing viewed down the *b* axis.

The photophysical properties of several **H1**–**H10** in CH_2Cl_2 are summarized in the Supporting Information (SI). In short, the UV-visible absorption and fluorescence of

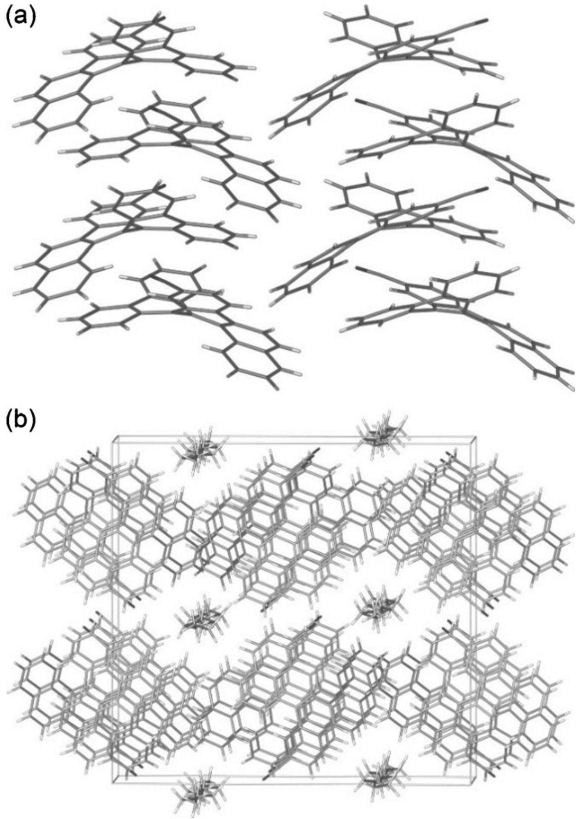


Figure 3. Crystal packing of **H7**·0.5 C_6H_{14}: a) a side view of stacks revealing extensive π–π interactions within each stack and weaker σ–π contacts (dashed lines) among the stacks; b) crystal packing viewed down the *a* axis.

selected helicenes **H1**–**H8** are in the range of 360–405 nm for λ_{abs} and 370–460 nm for λ_{em}.

All calculations were performed using the Gaussian 09 program package as discussed in the SI. In the design of materials for organic field effect transistors (OFETs), it is important to maximize electron mobility, which depends on many factors and can be enhanced if the reorganization energy (i.e., the difference in the geometries of the neutral and oxidized forms) is minimized.

A simple way to evaluate the effect of substituents at reorganization energies is to examine the HOMO structure. If a substituent is placed next to a node, then it will not have a large effect on reorganization energy. In contrast, if a substituent is not at the node and there is a lot of density at the respective position, it may have a large effect on the reorganization energies.[29]

Although DFT functionals do not always accurately predict electron affinities (EAs) and ionization potentials (IPs), the respective HOMO–LUMO gaps have relatively small errors.[30] Our DFT calculations predicted that methyl substitution (**H2**–**H4**) decreased the HOMO–LUMO gap relative to the unsubstituted **H1**. Furthermore, translocating the methyl group's position from carbon 1 to carbon 16 to carbon 18 progressively lowered the HOMO–LUMO gap by 0.04 eV. Importantly, both frontier MOs are fully delocalized through the π-framework, illustrating that bending does not prevent conjugation throughout the extended polyaromatic system (Figure S5a in SI).

The calculated effect of peripheral incorporation of heteroatoms (S, N) into the fused helicene, **H5** suggests large geometric and electronic changes—the presence of a nitrogen lone pair planarizes the respective fjord region in a favorable hydrogen bonding interaction (2.2 Å) with the proximal aromatic C–H. Electronically, the HOMO–LUMO gap is relatively attenuated (2.01 eV) with the HOMO significantly localized to the sulfur containing fused phenanthrene unit (see Figure S5b).

In conclusion, we describe a versatile method for the synthesis of complex, fused functionalized helicenes in high chemical yield. One of the key building blocks is provided by the selective Sn-mediated cyclization of aromatic *ortho*-enynes.[24] Sonogashira coupling followed by ICl-induced cyclization provide an iodinated precursor for the final photocyclization in yields consistently exceeding 80 %. The dehydrohalogenative photocyclization of iodinated *o*-terphenyls is viable and offers an efficient synthetic route to 4,5- and 5,5-fused double helicenes with differently substituted aromatic peripheries. The crystal packing is strongly influenced by the peripheral substituents, suggesting that their presence can be leveraged to impact photophysical and electrochemical properties of these materials.

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Keywords: alkynes · helicenes · photocyclodehydroiodination

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[25] The presence of copper in the Sonogashira reaction catalyzed the formation of homocoupling products of the terminal alkyne. For substrates **A1**–**A4**, we were unable to separate the homocoupled product from the desired internal acetylene products.

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