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Helicenes from Diarylmaleimides

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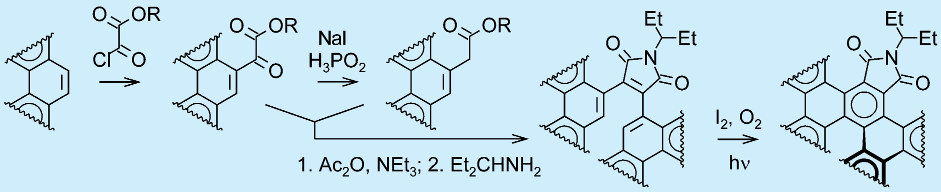
S *Supporting Information*



ABSTRACT: Perkin condensations of arylglyoxylic acids with arylacetic acids, followed by the addition of alkylamine, yield diarylmaleimides in a one-pot procedure. The arylglyoxylic acids are obtained by arene acylation with $ClCOCO_2Et$ and reduced with NaI and hypophosphorous acid to the arylacetic acids. With 2,7-di-*tert*-butyl-pyren-4-yl or chrysen-6-yl as the aryl, photocyclodehydrogenation of the diarylmaleimides yields substituted helicenes which can be reduced to stable anions. The helicenes combine bathochromically shifted absorption with hypsochromically shifted fluorescence with respect to their precursors.

Extended polycyclic arenes attract ever growing interest due to their optoelectronic properties, which with increasing size approach those of graphene.[1] In contrast to graphene, large discrete-size arenes allow the tuning of their electronic properties by the incorporation of electron-donating or -withdrawing substituents at their rim. But the synthetic accessibility and the technological utility of large polycyclic arenes are limited by their insolubility that quickly increases with size. For example, we recently found that already moderate-sized diperylenoanthracene-tetracarboxdiimide **1** (Figure 1), albeit bearing four long *n*-undecyl alkyl chains, is so poorly soluble even in chlorinated solvents that a satisfactory ^1H NMR spectrum could only be obtained at 130 °C,[2] whereas in perylene-tetracarboxdiimide **2** four ethyl substituents are sufficient to impart good solubility in chlorinated solvents at room temperature. An evident way out of this solubility dilemma and toward very large yet highly processable arenes is the avoidance of planar, well stacking, and thus poorly soluble systems by the introduction of twist: indeed, we observed that nonplanar polycyclic arene **3** shows good solubility even in cold toluene despite its size and the presence of only three *tert*-butyl substituents.[3]

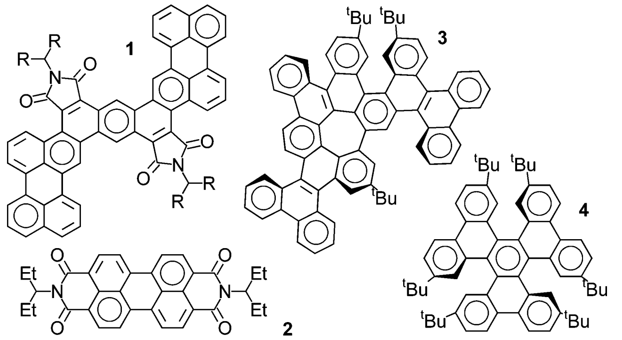


Figure 1. Planar aromatic diimides with limited solubility (left) and nonplanar aromatic hydrocarbons with excellent solubility (right). R = *n*-undecyl.

Highly congested triply helicenic structures such as **4** are efficiently accessible by intramolecular Scholl reactions,[4] but this chemistry precludes the presence of many electronically interesting substituents. On the other hand, we established that imides such as **1** are straightforwardly accessible from unsubstituted polycyclic arene precursors via Friedel–Crafts acylation followed by glyoxylic Perkin condensation with a bromoarylacetic acid and ring closure by Pd-assisted dehydrobromination.[2]

The photocyclization of stilbene-type compounds including diarylmaleimides is an established and efficient approach to helicenes,[5] and therefore we wondered whether the glyoxylic Perkin reaction[6] followed by photocyclization could offer a fast and straightforward approach to highly nonplanar structures such as **4** but with electronically desirable imide substituents such as in **1**. We therefore set out to synthesize symmetrical helicenedicarboximides from accessible polycyclic arenes via the corresponding arylglyoxylic acids.

Because of inherent regioselectivity challenges addressed ever since the first helicene photosyntheses,[5] polycyclic aromatic substrates for the Friedel–Crafts acylation with $ClCOCO_2Et$ should meet two requirements in order to provide an unambiguous access to helicenes: The most reactive substitution position should have only one neighboring hydrogen-

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bearing carbon in order to offer an unequivocal final photocyclization geometry, and this carbon to be photodehydrogenated should be the *α*-position of a naphthalene subunit to ensure that at least a [5]helicene is formed on cyclization.

Pyrene and perylene are among the most ubiquitous polycylic arenes in optics and electronics and satisfy the first of these two requirements: Both the reactive 1-position in pyrene and the reactive 3-position in perylene are adjacent to neighboring rings. However, they fail the second criterion, as no further benzene ring is present beyond the neighboring CH. But pyrene undergoes *tert*-butylation in positions 2 and 7, redirecting Friedel−Crafts acylation onto position 4,[7] which satisfies both criteria, while the *tert*-butyl group in position 7 ensures that photocyclization cannot go beyond the targeted [5]helicene to give a planar benzo[*ghi*]perylene subunit. Indeed, 2,7-di-*tert*-butylpyrene **5** reacts with $ClCOCO_2Et$ to yield the 4-glyoxylic ester **6** in the presence of $ZrCl_4$, a Lewis acid which we found previously to give cleaner Friedel−Crafts acylations than $AlCl_3$ and no concomitant glyoxylic ester hydrolysis.[2] Saponification with $NaHCO_3$ yields the glyoxylic acid **7** (Figure 2). Basic hydrolysis is to be preferred over acidic hydrolysis, as we found that prolonged heating with sulphuric acid in acetic acid leads to decarbonylation to the carboxylic acid, in agreement with the reported conversion of phenylglyoxylic acid to benzoic acid.[8] ^{13}C NMR spectroscopy is crucial for the differentiation of arylglyoxylic acids and esters such as **7** and **6** from their arylcarboxylic analogs that might have formed by carbonyl cleavage, as the second carbonyl signal at *ca.* 190 ppm is very characteristic.

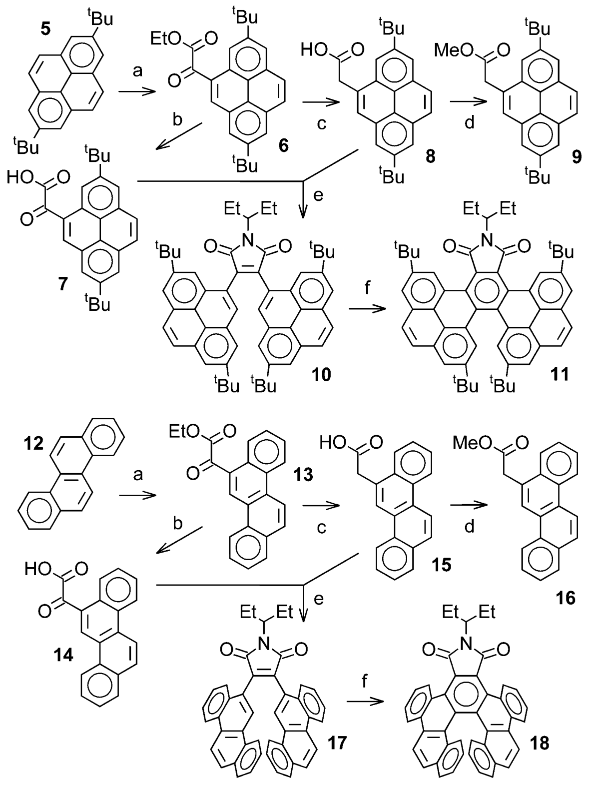

Figure 2. Synthesis of helicene-dicarboximides via glyoxylic Perkin reactions. (a) $ClCOCO_2Et$, $ZrCl_4$, DCM, 25 °C, 16 h, 61%/81%; (b) $NaHCO_3$, H_2O, EtOH, reflux, 2 h, 100%/97%; (c) NaI, H_3PO_2, H_2O, AcOH, reflux, 6 h, then addition of $MeSO_3H$, reflux, 64 h, 98%/94%; (d) MeOH, H_2SO_4, reflux, 16 h, 68%/91%; (e) NEt_3, Ac_2O, dioxane, reflux, 3 h, then addition of Et_2CHNH_2, reflux, 16 h, 75%/68%; (f) I_2, O_2, PhMe, reflux, 16 h/64 h, 60%/68%.

Although the Wolff−Kishner reduction of arylgloxylic acids such as 5-acenaphthylglyoxylic acid to the corresponding acetic acid has been reported,[9] the recent reports by Milne et al. of the reduction of phenylglyoxylic acid to phenylacetic acid with phosphorous acid and catalytic sodium iodide,[10] and by Hicks et al. of the reduction of alkyl aryl ketones to alkylarenes with hypophosphorous acid and catalytic iodine,[11] led us to search for a gentler approach than the Wolff−Kishner reaction by combining the two latter procedures. Indeed, we found that treatment of the glyoxylic ester **6** with hypophosphorous acid and sodium iodide in refluxing acetic acid, with methanesulphonic acid added to ensure complete hydrolysis, leads directly to the corresponding acetic acid **8**, which crystallizes in nearly pure form from the reaction mixture upon cooling to room temperature. Acidic esterification leads to the methyl ester **9**.

We previously reported that the glyoxylic Perkin reaction can be coupled in a one-pot procedure with basic esterification of the formed diarylmaleic anhydride, yielding the corresponding dialkyl ester directly.[2] We now find that imides can likewise be directly obtained, if excess alkylamine is added to the reaction mixture after the completion of the Perkin condensation. Dipyrenylmaleimide **10** is thus obtained in 75% yield from **7** and **8** in a one-pot procedure. To our delight, the cyclization of yellow **10** proceeded efficiently in refluxing toluene in the presence of iodine and air, yielding the red [5]helicene **11** overnight in 60% yield, simply using a conventional 200 W light bulb externally.[12] This photooxidation leads to the formation of an additional aromatic sextet in the Clar structure[13] of **11** compared to **10** (Figure 2), which may be a helpful driving force in the reaction.

Compared to other synthetic approaches to imide-functionalized helicenes, such as the Diels−Alder addition of a maleimide to 3,4,3′,4′-tetrahydro-1,1′-binaphthyl followed by oxidative aromatization (3% overall yield),[14] and compared to the four-step synthesis of photocyclizable nonalkylated maleimides from 5-amino-1,4-diaryl-1,2,3-triazoles,[15] the Perkin/photocyclization approach appears not only more general but also more efficient. Compared to recently reported photocyclizations of pyrenyl-naphthyl-ethylenes to [4] and [5]helicenes without imide substituents,[16] the photocyclization to **11** proceeds with greater yield and speed (and no need for a Cu-based sensitizer), which may be attributed to the greater stability and electron-withdrawing effect of the maleimide bridge.

11 shows good solubility in chlorinated solvents, and single crystals suitable for structure analysis could be obtained by diffusion of methanol into a DCM solution. The crystals are racemic; i.e., no separation of enantiomers is observed upon crystallization, albeit this is reported for other helicenes.[5] While the outer phenanthrene moieties in the two pyrene blades are nearly undistorted and planar, the bulk of the helical distortion is localized in the three inner benzene rings, with a central torsion angle along the three inner bonds of *ca.* 35° (Figure 3).

To test whether higher helicenes can be accessed by our glyoxylic approach with similar ease, we looked for a substrate prone to yield a [7]helicene. Although phenanthrene reacts in Friedel−Crafts acylations mainly in the 3-position suitable for [7]helicene construction,[17] we preferred chrysene **12**, because its regioselectivity in acylations is reported to be superior to

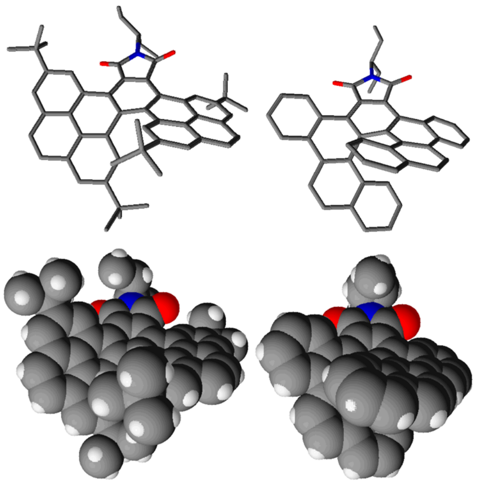

Figure 3. Crystallographic structures of pyrene-derived [5]helicene **11** and chrysene-derived [7]helicene **18** in stick (top, hydrogen atoms omitted) and calotte (bottom) representations.

phenanthrene,[17] and because no isomeric alternative to helicene formation is possible in the photocyclization.

The acylation of chrysene with $ClCOCO_2Et$ and $ZrCl_4$ is indeed highly regioselective and yields the expected 6-glyoxylic ester **13**, which is saponified to the glyoxylic acid **14** or reduced to the acetic acid **15** with the same ease as in the case of the pyrene series. **15** with sulphuric acid in refluxing methanol gives the methyl ester **16**. One-pot Perkin coupling of **14** and **15** plus imidification yields the dichrysenylmaleimide **17** in 68% yield.

Under similar conditions, the photoreaction of yellow **17** to the orange [7]helicene **18** proceeds more slowly than the cyclization of **10** to **11** in the pyrene series: after 3 days of reaction, besides a yield of 68% of **18**, traces of starting material **17** are still present and have to be separated by column chromatography. As in the case of **11**, the formation of **18** from **17** leads to a Clar structure[13] with an additional aromatic sextet in the newly formed six-membered ring (Figure 2).

Albeit not bearing solubility-enhancing *tert*-butyl groups like **11**, **18** is equally soluble in chlorinated solvents and yielded racemic crystals suitable for X-ray analysis by methanol diffusion. The *ca.* 36° inner torsion angle of **18** is nearly identical to that of **11**, showing that the two inward-pointing *tert*-butyl groups of **11** are roughly equivalent to the two terminal benzene rings of **18** in their effect on the helical distortion. In both **11** and **18**, the chirality of the individual molecule is expressed in both the ^1H and ^{13}C NMR spectra, where the two ethyl branches of the alkyl substituent are differentiated.

The absorption spectra are shifted bathochromically by about 50 nm upon cyclization of **10** to **11** and of **17** to **18**. Both maleimide precursors and both final helicenes are characterized by a broad plateau-like long wavelength absorption band of moderate intensity (Figure 4). Swallow-tail imides of condensed arenes are known to show intense fluorescence in solution,[18] and **11** and **18** are no exception in this respect. Astonishingly, albeit absorbing at higher wavelengths, both helicenes show their fluorescence maxima at lower wavelengths than their maleimide precursors. This striking reduction in Stokes shifts illustrates that conformational relaxation of the excited state prior to emission is much more restricted in the rigidified helicenes than in their flexible precursors.

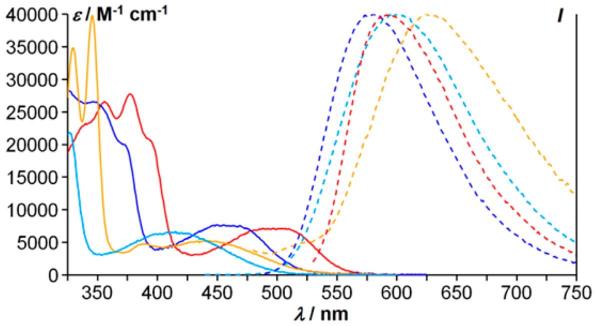

Figure 4. Absorption (continuous lines, left) and normalized fluorescence (dashed, right) spectra of **10** (orange, excitation at 460 nm), **11** (red, 510 nm), **17** (turquoise, 420 nm), and **18** (blue, 470 nm) in chloroform (20 μM).

The anodic and cathodic electrochemistry of **11** and **18** were evaluated by differential pulse voltammetry (DPV) and cyclic voltammetry (CV) in DCM. **11** has a reversible reduction at −1.67 V (all potentials are given vs ferrocene/ferrocenium (Fc/Fc^+)) and a reversible oxidation process at +0.85 V. **18** likewise shows a reversible reduction at −1.62 V. However, an irreversible oxidation at 1.15 V suggests that the radical cation of **18** is unstable. Both compounds thus exhibit their first reduction and oxidation potentials within the electrochemical window of DCM, which allows direct comparison of the electrochemical band gap with the optical band gap derived from the absorption spectra. With the energy level of Fc/Fc^+ at 4.8 eV below vacuum, voltammetry yields highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of $E_{\mathrm{HOMO}}(\mathbf{11}) = -5.65$ eV, $E_{\mathrm{LUMO}}(\mathbf{11}) = -3.13$ eV, $E_{\mathrm{HOMO}}(\mathbf{18}) = -5.80$ eV, and $E_{\mathrm{LUMO}}(\mathbf{18}) = -3.18$ eV and electrochemical band gaps of $\Delta E_{\mathrm{LUMO-HOMO}}(\mathbf{11}) = 2.52$ eV and $\Delta E_{\mathrm{LUMO-HOMO}}(\mathbf{18}) = 2.62$ eV. As the LUMO energies of **11** and **18** are nearly identical, the difference in band gap can be attributed primarily to the difference in HOMO energies.

From the absorption onset wavelengths (Figure 4) of *ca.* 560 nm for **11** and *ca.* 520 nm for **18**, optical band gaps of $\Delta E_{\mathrm{opt}}(\mathbf{11}) = 2.21$ eV and $\Delta E_{\mathrm{opt}}(\mathbf{18}) = 2.38$ eV are obtained. The differences between the electrochemical and optical band gaps of 0.31 eV for **11** and 0.24 eV for **18** can be identified as the exciton binding energies in the neutral excited species.[19]

In summary, we have found that our synthetic approach based on the one-pot reduction and hydrolysis of arylglyoxylic esters with hypophosphorous acid and iodide to arylacetic acids and their glyoxylic Perkin reaction coupled with *in situ* imidification and subsequent photocyclization can lead quickly and efficiently from planar polycyclic arenes to alkylimide-substituted helicenes, which exhibit strongly enhanced solubility compared to planar arene analogues of similar size and substitution. They show considerably smaller Stokes shifts than their maleimide precursors and form stable anions upon electrochemical reduction.

This approach can be extended to other dicarboxylic derivatives such as diesters and is also intrinsically suitable for the buildup of nonsymmetric helicenes because the photocyclized diarylmaleimide is built dissymmetrically from two complementary building blocks, the arylglyoxylic acid and the arylacetic acid, whose aryl parts need not be identical. If interest is vested in enantiomer separation or enantioselective synthesis of helicenes, the use of homochiral amines in the post-Perkin imidification may be an attractive option. If larger nonplanar and soluble carboxy-functionalized arenes are desired, suitable bifunctional building blocks, i.e. arylene-diglyoxylic and -diacetic acids satisfying our two design criteria for unambiguous helicene buildup, are to be targeted. A possible limitation of our approach is the general requirement of dilute solutions for photocyclizations, limiting the quantities of obtainable material per solvent volume in the final synthetic step.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic structures, electrochemical studies, synthetic procedures, ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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