Acenes

International Edition: DOI: 10.1002/anie.201812418
German Edition: DOI: 10.1002/ange.201812418

Dodecaphenyltetracene

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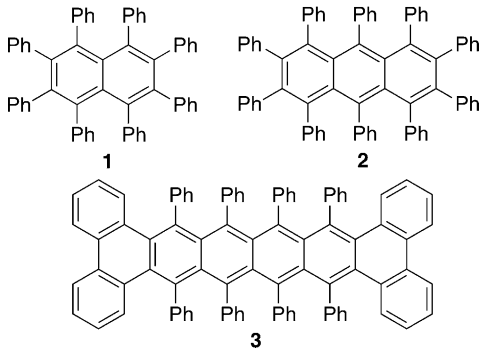
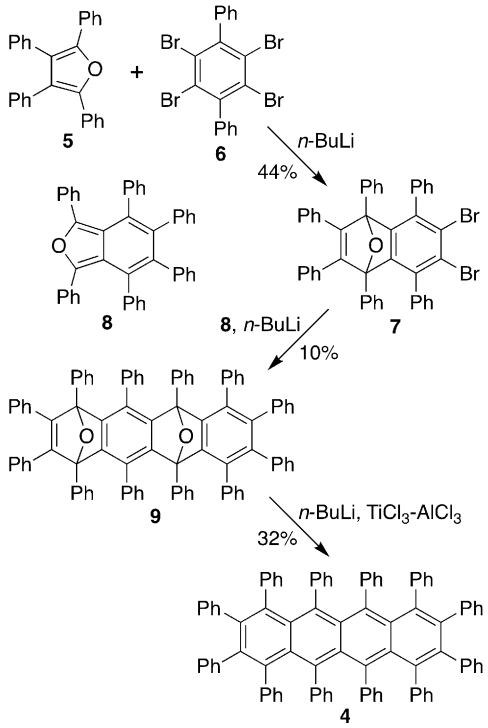
Abstract: *Dodecaphenyltetracene (**4**), the largest perphenylacene yet prepared, was synthesized from known tetraphenylfuran, hexaphenylisobenzofuran, and 1,2,4,5-tetrabromo-3,6-diphenylbenzene in three steps. The X-ray structure of the deep red, highly luminescent **4** shows it to be a D_2-symmetric molecule with an end-to-end twist of 97°. The central acene is encapsulated by the peripheral phenyl substituents, and as a result, the molecule is relatively unreactive and even displays reversible electrochemical oxidation and reduction.*

More than 20 years ago we reported the synthesis of octaphenylnaphthalene (**1**) and decaphenylanthracene (**2**).[1] Both molecules are twisted acenes,[2] and **2** displays an end-to-end twist of 63°. Much more highly twisted polycycles have since been prepared by benzannulation of the ends of acenes,[2] with the most recent "world record holder" being hexacene **3**, which displays an astonishing 184° end-to-end twist.[3]



However, all prior attempts to prepare the longer perphenylacenes dodecaphenyltetracene[4] and tetradecaphenylpentacene[5,6] met with failure. We now report the synthesis, spectra, and crystallographic characterization of the elusive dodecaphenyltetracene (**4**, Scheme 1).

Treatment of a cold solution of tetraphenylfuran[7] (**5**) and 1,2,4,5-tetrabromo-3,6-diphenylbenzene[5] (**6**) with 1.3 equivalents of *n*-butyllithium gave the single aryne adduct, the dibromoepoxynaphthalene **7**, in 44% yield. A similar treatment of **7** and hexaphenylisobenzofuran[8] (**8**) gave the diepoxytetracene **9** in only 10% yield, no doubt due to a greater steric impediment to this second aryne addition. The two oxygen atoms in the product were reduced away by treatment of **9** with a mixture of $TiCl_3$-$AlCl_3$ and *n*-butyllithium to give deep red **4** in 32% yield. However, a similar synthetic approach failed to yield tetradecaphenylpentacene.[9]



Scheme 1. Synthesis of dodecaphenyltetracene.

Solutions of dodecaphenyltetracene are magenta with a longest-wavelength absorption at 566 nm, a red shift of about 100 nm with respect to that of tetracene itself.[10] Compound **4** is also strongly luminescent, with a maximum emission at 613 nm and $\Phi = 0.12$ (Figure 1).

Single crystals of **4** suitable for X-ray analysis[11] were obtained upon evaporation of a solution in $CHCl_3$/EtOAc. Compound **4** crystallized in the space group *C*2 (No. 5) with $Z = 4$, and the asymmetric unit contains two independent half molecules of **4**. Therefore, the structure contains two crystallographically independent tetracenes, each of which possesses exact C_2 symmetry and approximate D_2 symmetry in the crystal. The molecular structure of one of these molecules is illustrated in Figure 2.

The tetracene core of compound **4** is smoothly twisted, with overall end-to-end twists[2] of 98(1)° and 96(1)° for the

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Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.201812418.

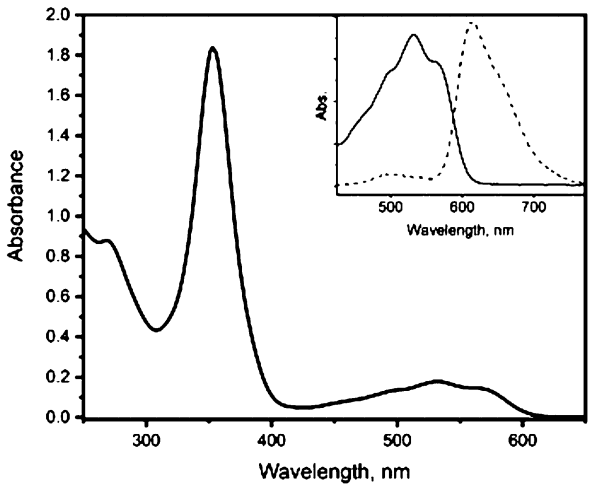

Figure 1. UV spectrum (CH_2Cl_2) of a 3.2×10^{-5} M solution of compound **4**. Inset: Luminescence of **4** (CH_2Cl_2) with excitation at 410 nm. The solid trace is the absorbance (an expansion of part of the full spectrum), and the dotted trace is the luminescence. The intensities of both are in arbitrary units so that the peaks are of roughly the same height.

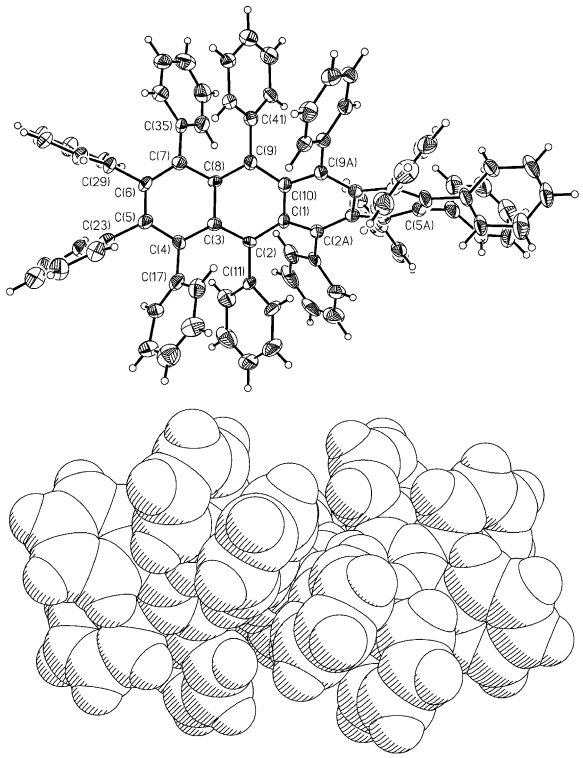

Figure 2. Molecular structure of dodecaphenyltetracene (**4**). Thermal ellipsoids are set at 50% probability.

two independent molecules, and it is obviously the most twisted perphenylacene so far prepared. Also significant is the "picket fence" of phenyl substituents, roughly perpendicular to, and out of conjugation with the tetracene, which essentially encapsulates the acene in an inert hydrocarbon sheath (see Figure 2). For this reason, compound **4**, like decaphenylanthracene (**2**),[12] displays fully reversible electrochemistry, with oxidation and reduction observed at +0.69 V and −1.50 V, respectively, versus Ag/AgCl (see the Supporting Information). Nevertheless, compound **4** is not completely unreactive, and solutions allowed to stand in the presence of air and light undergo slow decomposition to colorless oxidation products, as we have observed previously for other deeply-colored twisted acenes.[5,13]

The conformation of compound **4** is chiral, but it is unlikely to be configurationally stable under ordinary conditions. As with other twisted acenes, racemization is a multistep process with relatively modest barriers,[14] in contrast to the helicenes, where racemization occurs via a single, difficult step.[15] At the AM1 level of theory,[16] a four-step racemization pathway was identified in which the highest barrier ($\Delta G^{\ddagger}_{rac}$) is only 17.3 kcal mol^{-1} (see the Supporting Information). If correct, this corresponds to a half-life of less than a second at room temperature.

Dodecaphenyltetracene (**4**) is the largest perphenylacene yet prepared. Simple steric crowding forces the tetracene to adopt a twisted ribbon conformation, but, unlike the majority of twisted polycyclic aromatic compounds,[2] compound **4** lacks rings or functional groups conjugated to the central acene, such as the benzannulations in **3**. In **4**, the phenyl substituents are nearly orthogonal to the rings of the tetracene core at their points of attachment. Accordingly, the electronic structure of the central acene is largely unaltered, as may be seen from the UV spectrum of **4**, which resembles that of tetracene itself except for the expected red shift.

Acknowledgements

This work was supported in part by National Science Foundation Grants CHE-1265507, CHE-1762452, and MRI-1228232, and Louisiana Board of Regents Grant LEQSF-(2002-03)-ENH-TR-67 (the latter two for instrumentation in the Tulane X-ray diffraction facility).

Conflict of interest

The authors declare no conflict of interest.

Keywords: acenes · polycyclic aromatic hydrocarbons · polyphenyl aromatic compounds

How to cite: *Angew. Chem. Int. Ed.* **2019**, *58*, 2831–2833
Angew. Chem. **2019**, *131*, 2857–2859

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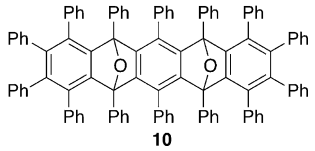
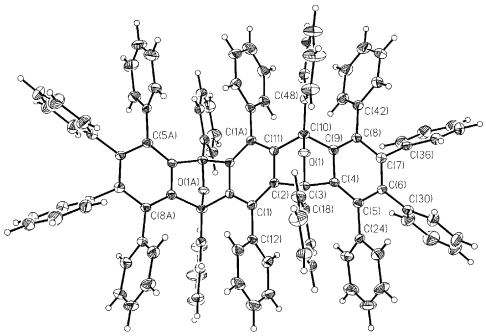
[9] When the synthesis illustrated in Scheme 1 is repeated using compound **8** as the diene for both aryne additions, the diepoxide **10** is obtained in an abysmal 0.6% yield. The molecular structure of **10** was confirmed by X-ray analysis (illustrated below), but all attempts to remove the oxygen atoms have failed. These attempts included reduction with $TiCl_3$/*n*-butyllithium,[5] Zn/HOAc,[1] and $SnCl_2$,[3] all of which have been used previously to prepare highly twisted acenes from oxygenated precursors.



10



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[11] X-ray crystal structure determination for **4**: Formula $C_{90}H_{60}{\cdot}CHCl_3$, $M = 1260.74$, crystal size $0.119 \times 0.102 \times 0.078$ mm, monoclinic, *C*2, $a = 23.1292(11)$ Å, $b = 17.7226(9)$ Å, $c = 21.4625(11)$ Å, $\beta = 121.517(2)$, $V = 7499.9(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.117$ Mg m^{-3}, $\mu = 1.437$ mm^{-1}, Cu Kα radiation ($\lambda = 1.54178$ Å), $2\theta_{max} = 146.274°$, $T = 150(2)$ K. 27758 reflections were measured, the structure was solved by direct methods, and it was refined by full-matrix least-squares on F^2. $R(F) = 0.1108$, $wR(F^2) = 0.2881$, and $S = 1.034$ for 8685 reflections with $I > 2\sigma(I)$, and $R(F) = 0.1352$, $wR(F^2) = 0.3082$, and $S = 1.054$ for 11421 unique reflections, 831 parameters, and 725 restraints. The residual electron density ranged from −0.51 to 0.66 *e* A^{-3}. CCDC 1875175 and 1875176 (**4**, **10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
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Manuscript received: October 29, 2018
Accepted manuscript online: January 9, 2019
Version of record online: February 5, 2019

