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Oligotwistacene

Synthesis and Structure Characterization of a Stable Nonatwistacene**

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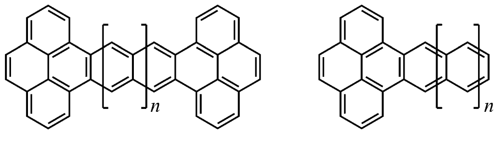
As an important class of organic electronic materials, acenes have already received much attention in both fundamental investigations and practical applications.[1–5] Although theoretical modelling and calculations suggest that larger acenes can have a singlet disjointed biradical character or an antiferromagnetic character in the ground state,[4] there are few successful studies on the synthesis and experimental characterization of larger acenes (> 7 repeating benzo units). Owing to difficult multistep synthetic approaches, tedious separation, poor solubility, and extreme instability (sensitivity to light, oxygen, and polymerization),[1–3,6] linear polyacenes remain challenging systems. In order to avoid these drawbacks and approach the larger stable acenes, several groups have reported successful results by selectively adding protecting groups, such as phenyl, fluoride, arylthio, or silylethyne, on the periphery of the conjugated acene frameworks to increase solubility and enhance stability.[1–3,5,7]

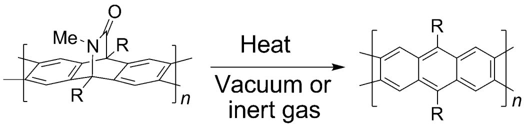
Our groups are particularly interested in acenes with rigid terminal pyrene units (Figure 1). The acene family containing rigid terminal pyrenes (or phenanthrenes) can be divided into two types:[6,8,9] double-terminal pyrenes (or phenanthrenes; type I, Figure 1) and single-terminal pyrene (or phenanthrene, type II, Figure 1). The non-bonding interactions between substituents (or even H atoms) on the twistacene backbone and the pyrene can cause the framework of the acenes to twist.[5,7a,8–10] We believe that this twist, together with selectively appended phenyl substitutents, offers enhanced protection of the larger acene molecules in this family from dimerization and oxidation. In fact, we have already reported several remarkably stable twisted acenes and heteroacenes containing single/double-terminating pyrene units.[5,7a,9,11]



Type I Type II

Figure 1. Twistacene structures.

Recently, we developed a clean reaction method to prepare the larger acenes and their derivatives in a pure state and in near quantitative yield from the corresponding precursors.[9,11] The key step in this strategy is a retro-Diels–Alder process involving the thermal elimination of lactam bridges from soluble acene precursors (Scheme 1). This method, together with the twist concept, led us to believe that a higher twistacene could be prepared. Herein we report the synthesis and characterization of 6,8,10,17,19,21-hexaphenyl-1.22,4.5,11.12,15.16-tetrabenzononatwistacene (**1**; Scheme 2).



Scheme 1. Clean reaction approach to higher acenes.

The desired precursor **2**, was obtained in 22% yield through a cycloaddition reaction between **3** and the aryne generated from **4** (Scheme 2; see the Experimental Section for full chemical names).[5a,11] A reaction to eliminate the bridge, performed in either diphenyl ether (sealed tube at 330 °C; Scheme 2) or the solid state, proved to be an efficient way to form compound **1**. Slowly cooling the diphenyl ether solution afforded cubic, dark-green crystals of **1**. These crystals are stable in air for more than five days without any protection.

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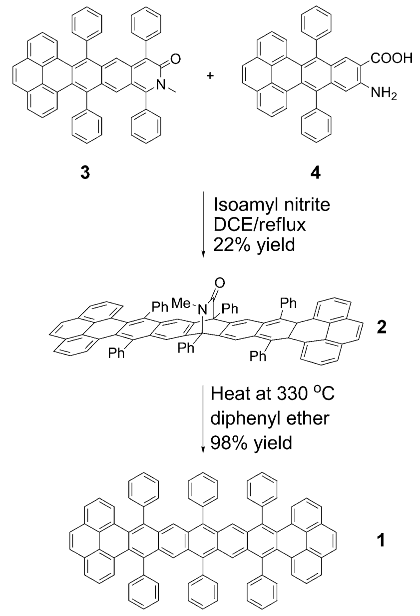

Scheme 2. Synthesis of 6,8,10,17,19,21-hexaphenyl-1.22,4.5,11.12,15.16-tetrabenzononatwistacene (**1**). DCE = 1,2-dichloroethane.

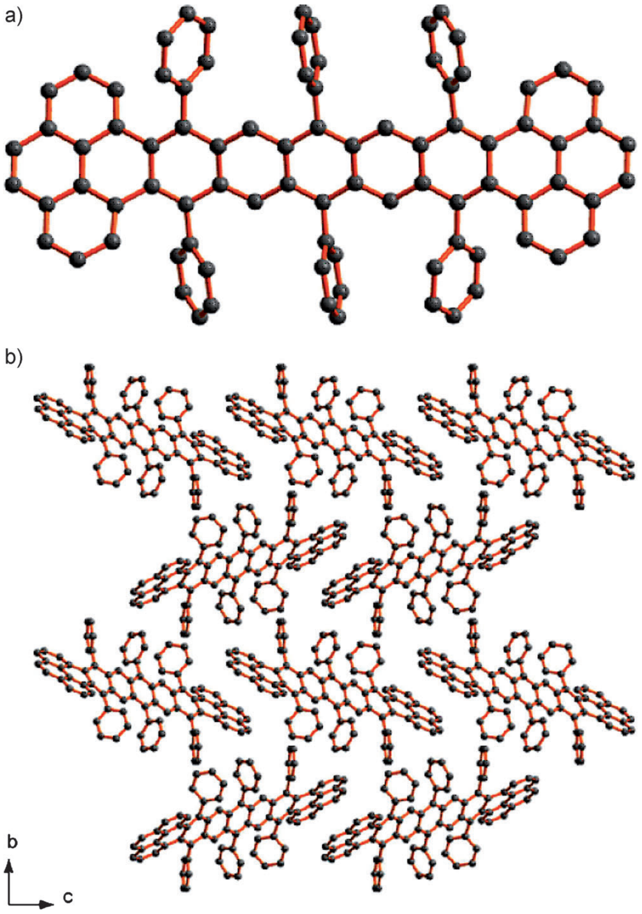

Figure 2. Single crystal analysis of **1**. a) One molecule unit. b) Molecular packing.

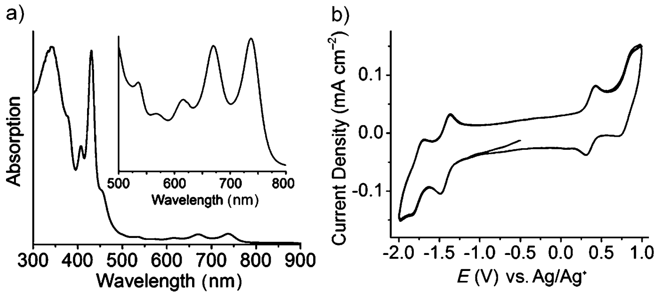

Figure 3. a) The UV–Vis absorption spectra of **1** in CH_2Cl_2. The inset shows the magnified spectrum. b) Cyclic voltammogram of **2** in 1,2-dichlorbenzene using tetrabutylammonium perchlorate as an electrolyte.

The structure of nonatwistacene **1** was clearly confirmed by X-ray crystallography (Figure 2).[17] Immediately apparent from the side-on view of the crystal packing of **1** (Figure 2b) is the presence of some twist to the nonacene π system. The twist angle is about 25.64°, which is larger than that of the heptacene analogue.[7a] The most prominent intermolecular interactions stabilizing the crystal packing are the π–π stacking (3.44 Å) interactions of the pyrene units (Figure 2b). The pentacene units, which are the main contributors to the electronic properties, do not exhibit strong π–π interactions. This arrangement makes compound **1** more stable.

The UV–Vis spectrum of **1** (measured in CH_2Cl_2), with the longest absorption λ_{max} at 739 nm (1.68 eV), is shown in Figure 3a. The bands in the finger region (580–800 nm) are characteristic of the acene family (inset in Figure 3a). Cyclic voltammetry of **1**, measured in 0.1M tetrabutylammonium perchlorate/1,2-dichlorobenzene (TBAP/ODCB; recorded at 150 °C), showed that the oxidation and reduction processes are chemically and electrochemically reversible (Figure 3b). The HOMO–LUMO gap calculated from the difference between the half-wave redox potentials ($E_{1/2}^{ox} = +0.30$ eV and $E_{1/2}^{red} = -1.42$ eV) is 1.72 eV. The $\Delta E_{\text{HOMO-LUMO}}$ corroborates the value of 1.68 eV derived from the UV–Vis data. Furthermore, these results place the HOMO–LUMO gap of **1** between that of heptacene (1.36 eV) and hexacene (1.84 eV),[1c,2a] which is much lower than that of pentacene (2.1 eV).[12]

Density functional theory (DFT) calculations were performed at the B3LYP/6-31G(d,p) level of theory[13,14] using the Gaussian09 program.[15] The geometry of **1** is fully optimized with a convergence criterion of 10^{-3} a.u. on the gradient and displacement and 10^{-6} a.u. on energy and electron density. Harmonic vibrational analyses show no imaginary frequency, indicating that the structure of **1** is a local minimum. The dipole-allowed vertical excitation in the gas phase was calculated by time-dependant DFT using the same basis set.[16] The first absorption peak, which has an excitation energy of 1.64 eV, is the electron excitation from HOMO to LUMO. The peak corresponds to the π–π* type transition, as shown in Figure 4, which is in good agreement with the experimental data (1.68 eV). Furthermore, the calculation demonstrates that the pyrene unit does contribute to the HOMO–LUMO gap.[9]

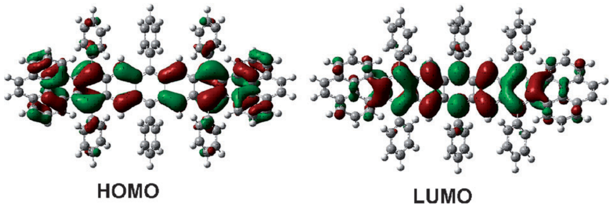

Figure 4. Wave function plot for the HOMO and LUMO of **2**.

In conclusion, we have successfully synthesized and fully characterized the novel, stable, green crystalline 6,8,10,17,19,21-hexaphenyl-1.22,4.5,11.12,15.16-tetrabenzo-nonatwistacene **1** through a clean reaction strategy. Currently, nonatwistacene **1** is the longest acene type I system and possesses a low HOMO–LUMO gap, which is close to that reported for hexacene. Crystallographic analysis revealed the presence of the conjugated nonatwistacene chromophore with a twisted topology. We are currently exploring the potential electronic applications of this new nonatwistacene.

Experimental Section

2-Methyl-1,4,6,13-tetraphenyl-7:8,11:12-bisbenzoanthro[g]-isoquinolin-3(2*H*)-one (**3**)[11] and 3-amino-5,12-diphenyl-6:7,10:11-bisbenzo-tetracene-2-carboxylic acid (**4**)[5a] were synthesized according to the reported procedures. All solvents were used without further purification.

Synthesis of *N*-methyl-6,8,10,17,19,21-hexaphenyl-1.22,4.5,11.12, 15.16-tetrabenzo-8.19-bicyclo-1′′′′′-aza-2′′′′′-one-nonacene (**2**): A solution of 3-amino-5,12-diphenyl-6:7,10:11-bisbenzotetracene-2-carboxylic acid (**4**; 45 mg, 0.085 mmol) in 1,2-dichloroethane (DCE; 10 mL) was added dropwise to a refluxing solution of 2-methyl-1,4,6,13-tetraphenyl-7:8,11:12-bisbenzo-anthro[g]isoquinolin-3(2*H*)-one (**3**; 40 mg, 0.057 mmol) and isoamyl nitrite (40 mg, 34 mmol) in DCE (5 mL). After 1 h, DCE was removed under reduced pressure and the crude residue was purified using silica-gel column chromatography with methylene chloride followed by methylene chloride/diethyl ether (5:1) to afford **2** (28 mg, 22 %) as a light yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.14$ (s, 2H), 7.92 (m, 11 h), 7.69–7.59 (m, 6H), 7.47–7.29 (m, 31H), 2.92 (s, 3H). IR (DRIFT): $\tilde{\nu} = 3052$, 1681, 1442, 1313, 831, 720, 703, 539 cm^{-1}. MALDI-TOF MS: exact mass (M−[Me−N=C=O]+H) 1083.3882; calcd (M−[Me−N=C=O]+H) 1083.3913. Elemental analysis: found C, 92.44; H, 4.54; calcd C, 92.68; H, 4.68.

6,8,10,17,19,21-Hexaphenyl-1.22,4.5,11.12,15.16-tetrabenzo-nonatwistacene (**1**): The precursor, *N*-methyl-6,8,10,17,19,21-Hexaphenyl-1.22,4.5,11.12,15.16-tetrabenzo-8.19-bicyclo-1′′′′′-aza-2′′′′′-one-nonacene (**2**), was heated in diphenyl ether at 330 °C (sealed tube) for 4 h. After slowly cooling down, the dark-green crystals were collected (ca. 100 % yield). Mp: > 300 °C. Elemental analysis: found C, 95.17; H 4.46; calcd. C, 95.35; H, 4.65. MALDI-TOF MS: exact mass: 1083.3905; calcd. Mass: 1082.3913. IR (DRIFT, cm^{-1}): $\tilde{\nu} = 3054$, 1487, 1443, 1400, 1298, 830, 721, 690, 536.

Solution NMR spectra were taken on a Bruker ARX 500 spectrometer. Electrochemistry was carried out with a BAS 100 B/W potentiostat, employing a platinum button (diameter: 1.6 mm; area 0.02 cm^2), a platinum wire, and a 0.01 M $Ag/AgNO_3$ (Ag/Ag^+) as working, counter, and reference electrode, respectively. Tetrabutylammonium perchlorate (0.1 M) in 1,2-dichlorobenzene (ODCB) was used as an electrolyte. As compound **1** was not very soluble in ODCB at room temperature, cyclic voltammetry measurements were conducted at higher temperatures (ca. 150 °C).

X-ray crystal structure of **1** (CCDC 857476).[17] A single-crystal data set was collected at 103 K on a Bruker SMART APEX II CCD with graphite-monochromatized Mo K_α radiation ($\lambda = 0.71073$ Å). Data processing (APEXII and SMART) and absorption correction (SADABS) were accomplished by standard methods. The structure was solved by direct-methods using SHELXS-97 and refinement, with anisotropic displacement parameters, hydrogen atoms in the riding model approximation, and a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (0.064P)^2 + 0.376P]$ for $P = (F_o^2 + 2F_c^2)/3$, was on F^2 by means of SHELXL-97.

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Keywords: density functional calculations · organic electronic materials · retro-Diels–Alder reaction · synthesis design · twistacenes

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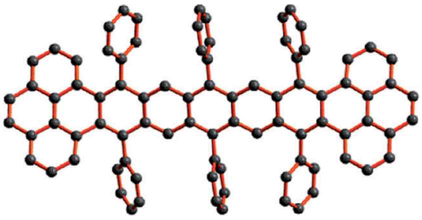
[17] CCDC 857476 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Oligotwistacene

J. Xiao, H. M. Duong, Y. Liu, W. Shi, L. Ji, G. Li, S. Li, X.-W. Liu, J. Ma, F. Wudl,* Q. Zhang* ______ ■■■■–■■■■

Synthesis and Structure Characterization of a Stable Nonatwistacene



A clean reaction strategy based on thermally eliminating lactam bridges from a soluble acene precursor through a retro-Diels–Alder reaction, led to the synthesis and characterization of a novel, stable, green crystalline 6,8,10,17,19,21-hexaphenyl-1.22,4.5,11.12,15.16-tetrabenzononatwistacene. An analysis of the single crystal structure of the nonatwistacene indicates that this molecule is twisted at an angle of 25.44°.