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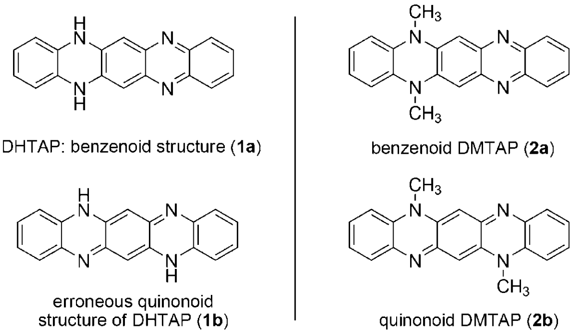
Benzenoid and Quinonoid Nitrogen-Containing Heteropentacenes

Qin Tang,[a] Jing Liu,[a] Hoi Shan Chan,[a] and Qian Miao*[a, b]



Scheme 1. Structures of dihydro-5,7,12,14-tetraazapentacene (DHTAP) and *N*,*N'*-dimethyldihydro-5,7,12,14-tetraazapentacenes (DMTAPs).

Nitrogen-containing heteroacenes are an interesting class of π-functional materials,[1] but they have been much less studied than oligoacenes, which are very important building blocks for organic electronics.[2,3] The recent interest in nitrogen-containing heteropentacenes has arisen from the opportunities of tuning the electronic structure, stability, solubility, and molecular packing by introducing nitrogen atoms into the backbone of pentacene.[4] Although some nitrogen-containing heteropentacenes have been known for over a century,[5] few of them were fully characterized structurally. Dihydro-5,7,12,14-tetraazapentacene (DHTAP), also known as fluorindine, is not only regarded as a small-molecule model for ladder polymers,[6] but also functions as an organic semiconductor in organic field effect transistors (OFETs).[7] The true structure of DHTAP is benzenoid (**1a** in Scheme 1) as determined by ^{1}H NMR spectroscopy.[8] However in most of the reports on DHTAP until recently, it was erroneously given a quinonoid structure (**1b** in Scheme 1).[9,10] This quinonoid structure was first proposed based on a belief that the absorption of DHTAP near 600 nm is not compatible with the benzenoid structure **1a**,[10] which has two nitrogen atoms connecting a phenazine ring and a benzene ring.[4a,8a] In connection with the debate on the structure of DHTAP, we have recently found that methylation of DHTAP allowed not only *N*-alkylation but also *C*-alkylation, and yielded both benzenoid and quinonoid heteropentacenes (**2a** and **2b** in Scheme 1). This finding led to an exploratory study on the molecular and electronic structures, molecular packing, and semiconductor properties of both benzenoid and quinonoid nitrogen-containing heteropentacenes as detailed below.

The synthesis of **2a** and **2b** is shown in Scheme 2a. A new method of condensing *o*-phenylenediamine and 2,5-dihydroxy-1,4-benzoquinone without solvents and acidic catalysts produced DHTAP in a good yield. Deprotonation of DHTAP with *n*BuLi followed by treatment with iodomethane yielded three products (**2a**–**c**), which were easily isolated by chromatography on silica gel.[11] Unlike the parent molecule DHTAP, **2a**–**c** are soluble in organic solvents, presumably due to the lack of hydrogen bonds in the solid state, and were completely characterized. The formation of **2c** involves both *N*- and *C*-methylation, indicating that the dianion of DHTAP has negative charges delocalized not only on nitrogen atoms but also on the neighboring carbon atoms through a series of resonance forms. The resonance forms of the DHTAP dianion that lead to **2a**–**c** are shown in Scheme 2b.[12] The intermediate **4**, which has a relatively acidic proton, is further deprotonated and methylated to yield **2c**.

In the ^{1}H NMR spectra of **2a** (see the Supporting Information) the protons of the two terminal benzene rings give rise to two groups of characteristic AA′XX′ patterns,[13] which are also found in the ^{1}H NMR spectrum of DHTAP and can be regarded as direct evidence for the benzenoid structure of **1a**.[8] In contrast, the protons of two terminal

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[a] Q. Tang, J. Liu, H. S. Chan, Prof. Dr. Q. Miao
Department of Chemistry, The Chinese University of Hong Kong
Shatin, New Territories, Hong Kong (China)
Fax: (+852) 26035057
E-mail: miaoqian@cuhk.edu.hk

[b] Prof. Dr. Q. Miao
Center of Novel Functional Molecules
The Chinese University of Hong Kong
Shatin, New Territories, Hong Kong (China)

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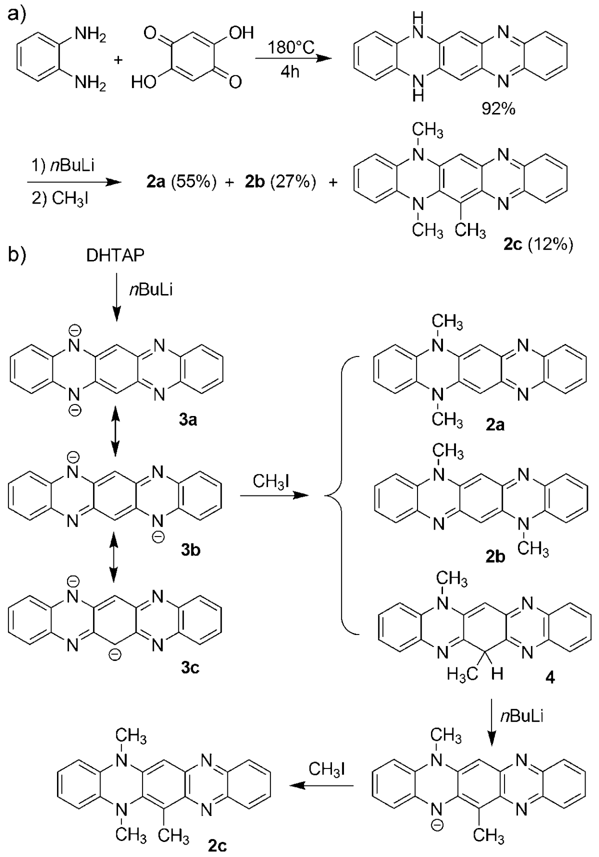


Scheme 2. a) Synthesis of **2a**–**c**; b) proposed mechanism for the formation of **2a**–**c**.

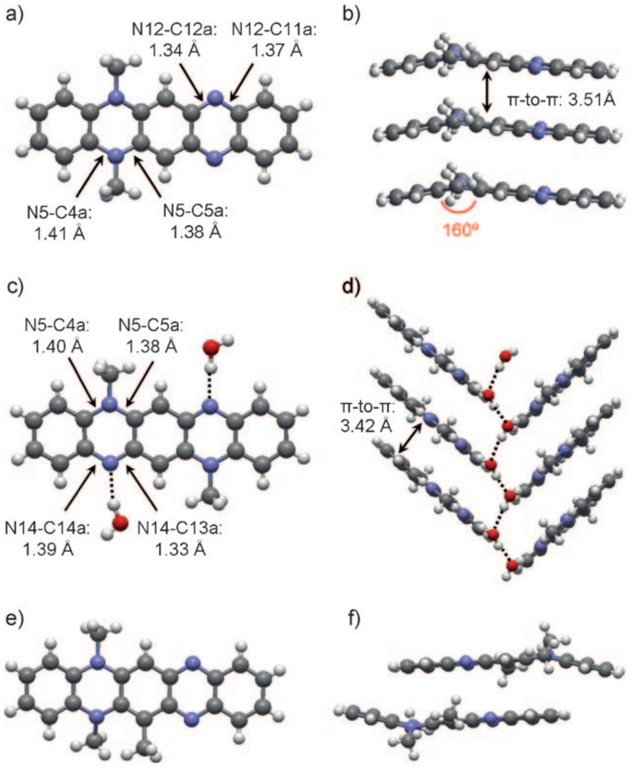
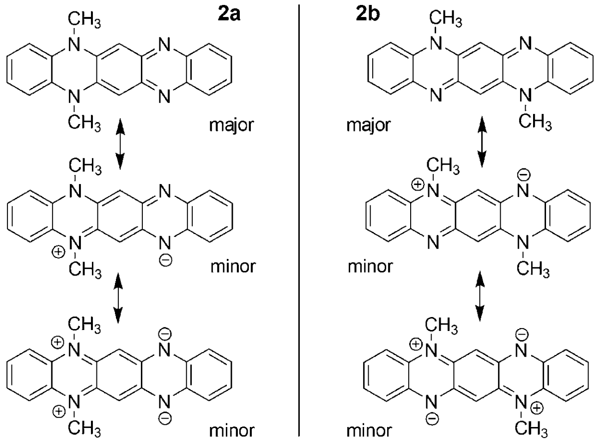


Figure 1. Crystal structures of **2a**–**c** showing: a) a single molecule of **2a** with bond lengths highlighted; b) π-stacks and the bending angle of **2a**; c) a single molecule of **2b** with H-bonds to two water molecules; d) a H-bonded chain of water molecules between two π-stacks of **2b** (H-bonds between water molecules are shown as dashed lines); e) top view of a single molecule of **2c**; f) side view of a stacked dimmer of **2c**.



Scheme 3. Resonance structures of **2a** and **2b**.

benzene rings of **2b** give rise to four peaks in the ^{1}H NMR spectra (see the Supporting Information) corresponding to a disubstituted benzene ring with two different substituents *ortho* to each other. The protons of the central ring of **2a** and **2b** show single peaks at $\delta = 6.67$ and 5.97 ppm, respectively, in agreement with the deshielding effect by the ring current of the benzenoid central ring of **2a**.

Crystals of **2a**–**c** were grown by slow evaporation from solutions in acetone. X-ray crystallography of these crystals reveals the structures and assemblies of the three molecules as shown in Figure 1.[14] The backbone of **2a** bends at the methylated nitrogen atoms with a bending angle of 160° as illustrated in Figure 1b. The N5–C5a bond (1.38 Å) is shorter than the N5–C4a bond (1.41 Å) and the corresponding N–C bond of *N,N'*-dimethyldihydrophenazine (1.41 Å),[15] revealing the partial double-bond character of the N5–C5a bond. The N12–C12a bond (1.34 Å) is shorter than the N12–C11a bond (1.37 Å), indicating the former has more double-bond character than the latter.[16] Therefore **2a** should be represented by a series of resonance contributors shown in Scheme 3 rather than a single Kekulé structure. Molecules of **2a** form infinite stacks in two directions with the phenazine planes being 3.51 Å apart from each other. Unlike **2a**, **2b** is essentially flat as found in the crystal structures shown in Figure 1c and 1d. The N14–C13a bond (1.33 Å) is significantly shorter than the N14–C14a bond (1.39 Å) in agreement with a double bond between the N14 and C13a atoms. The N5–C5a bond (1.38 Å) is shorter than the N5–C4a bond (1.40 Å), indicating the former has more double-bond character than the latter. This can be explained by the minor resonance contributors of **2b** shown in Scheme 3. Interestingly, water molecules, which come from the solvent of wet acetone, are found in the crystal lattice of **2b**. As shown in Figure 1c, one molecule of **2b** forms hydrogen bonds with two molecules of water. Molecules of **2b** assemble into stacks with a π–π distance of 3.42 Å, and water molecules are linked by hydrogen bonds to form a chain between the neighboring stacks of **2b**. Similar to **2a**, **2c** is also a bent molecule, and the two adjacent methyl groups are distorted to avoid steric repulsions. A stacked dimer of **2c** (Figure 1 f) is the unit of molecular packing in the crystal.

The quinonoid structure was misassigned to DHTAP because of a lack of knowledge on the electronic structure of benzenoid and quinonoid nitrogen-containing heteroacenes. Therefore the electronic structure of **2a** and **2b** was studied by using both experimental and computational methods. Both **2a** and **2b** are red in solution. A comparison of the absorption spectra of **2a** and **2b** is shown in Figure 2a. In the visible light range, **2a** exhibits a peak at 498 nm and a shoulder at 520 nm, whereas **2b** exhibits three peaks at 551, 512, and 479 nm. Although the longest-wavelength absorption peak of **2b** is red-shifted by about 50 nm in comparison with that of **2a**, the absorption edges of the two molecules are close to each other (ca. 565 nm for **2a** and ca. 575 nm for **2b**). From the absorption edge, the HOMO–LUMO gap is calculated to be 2.19 eV for **2a** and 2.16 eV for **2b**. The frontier molecular orbitals of **2a** and **2b** were calculated by using the hybrid density functional method B3LYP with a 6-31+G* basis set,[17] and is depicted graphically in Figure 2b. Like **2b**, **2a** has a delocalized highest-occupied molecular orbital (HOMO). However, the lowest unoccupied molecular orbital (LUMO) of **2a** mainly resides on the phenazine moiety. Cyclic voltammograms (CVs) of **2a** and **2b** (see the Supporting Information) in DMF exhibit one reversible oxidation wave and one reversible reduction wave. The half-wave oxidation potential versus ferrocenium/ferrocene is 0.21 V for **2a** and −0.01 V for **2b**, from which the HOMO energy levels of **2a** and **2b** are estimated as −5.01 eV and −4.79 eV, respectively.[18] The half-wave reduction potentials versus ferrocenium/ferrocene is −1.91 V for **2a** and −1.84 V for **2b**, from which the LUMO energy levels of **2a** and **2b** are estimated to be −2.89 eV and −2.96 eV, respectively. The HOMO and LUMO energy levels of **2a** obtained from CVs are in good agreement with the optical gap calculated from the absorption edge. However the electrochemical HOMO–LUMO gap of **2b** is about 0.3 eV smaller than its optical gap. The HOMO energy levels of **2a** and **2b** obtained from CVs correspond with the computed ones, whereas the LUMO energy levels obtained from CVs are lower than the computed ones. The above studies on the electronic structure of **2a** indicate that the N5 and N14 atoms have the lone pairs of electrons in effective conjugation with the adjacent phenazine ring although the molecule is bent at the two N atoms. Such conjugation leads to the HOMO and LUMO energy levels that are close to those of **2b**, and is consistent with bond lengths found in crystal structures. This finding appears an amendment to the previous understanding that the two NH units in nitrogen-containing heteropentacenes break the delocalization of the π system in the pentacene skeleton.[4a,8a,19]

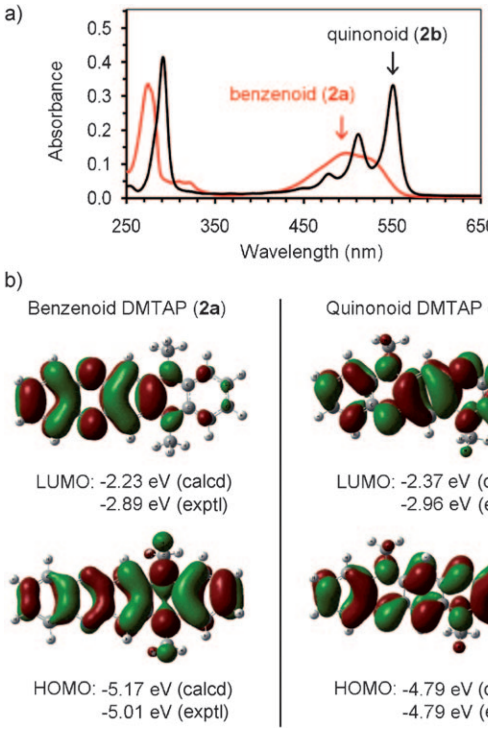


Figure 2. a) Absorption of **2a** and **2b** (3×10^{-6} M in THF); b) frontier molecular orbitals of **2a** and **2b**.

The studies on the crystal and electronic structure of **2a** and **2b** indicate that both the molecules self-assemble into stacks with intermolecular π-orbital overlap, and have delocalized HOMOs with energy levels accessible for charge injection, suggesting that **2a** and **2b** can function as p-type organic semiconductors.[20] Therefore, the two molecules were tested in organic field effect transistors (OFETs).[21] Flake- or needle-shaped thin crystals of **2a** and **2b** were grown by physical vapor transport (PVT),[22] and were placed on a SiO_2/Si substrate with pre-deposited drain and source electrodes of gold.[23] The resulting devices were bottom-contact OFETs with highly n-doped silicon as a gate electrode, a 300 nm thick layer of SiO_2 as dielectrics, and the semiconductor channel length in a range of 50 μm to 150 μm. A micrograph of such a type of device is shown in Figure 3a. It is

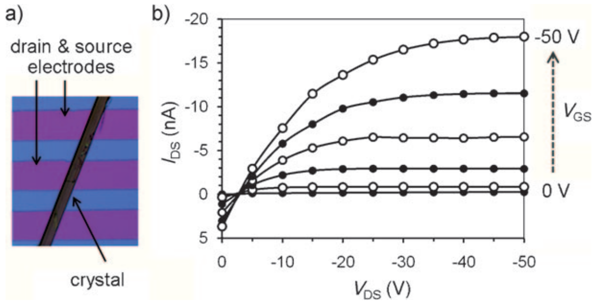


Figure 3. a) A micrograph of an OFET fabricated from a very thin crystal of **2b**; b) drain current versus drain voltage for the OFET of **2a** with an active channel of $L=150$ μm, $W=365$ μm.

found that both **2a** and **2b** behave as p-type semiconductors in OFETs. The typical *I–V* curves for the OFETs of **2a** are shown in Figure 3b, from which a field-effect mobility of $5\times 10^{-4}\,cm^2V^{-1}s^{-1}$ was measured in the saturation regime using the equation: $I_{DS}=(\mu WC_i/2L)(V_G-V_T)^2$, where I_{DS} is the drain current, μ is the field effect mobility, W is the channel width, L is the channel length, V_G is the gate voltage, V_T is the threshold voltage, and C_i is the capacitance per unit area ($11\,nF\,cm^{-2}$ for 300 nm SiO_2). In comparison, **2b** shows a lower field effect mobility of $1\times 10^{-4}\,cm^2V^{-1}s^{-1}$. The mobilities of **2a** and **2b** measured in this study appear lower than the one reported for DHTAP.[24] The low mobilities of **2a** and **2b** might be not intrinsic of the materials but limited by the poor contacts in the devices.

In summary, benzenoid and quinonoid nitrogen-containing heteropentacenes were successfully isolated and investigated. The complete characterization of **2a** and **2b** revealed π-electron delocalization in these polynuclear heterocycles and π-stacks in their molecular assemblies. These findings led to a better understanding of the electronic structures and clearly supported the benzenoid structure of DHTAP, which has been debated. It is found that both benzenoid and quinonoid nitrogen-containing heteropentacenes can function as p-type organic semiconductors. Furthermore, because the parent molecule DHTAP was regarded as a small-molecule model for a series of ladder polymers,[6] the findings presented in this report may also have implications for interesting ladder polymers.

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Keywords: acenes · electronic structure · heterocycles · self-assembly · semiconductors

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