A Potential Iterative Approach to 1,4-Dihydro-N-Heteroacene Arrays

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A new method for the synthesis of substituted 1,4-dihydrophenazines is reported and the structure of N-butyl-5-methyl-3-nitro-5,10-dihydrophenazine is proven by an X-ray single-crystal structure determination.

1. Introduction

Pentacene[1] has been investigated in organic electronics with fundamental studies on electronic properties,[1–3] optical properties,[4–6] and device physics (Figure 1).[1,12] However, it suffers from long-term stability because of its photo-oxidation and low thermal stability.[12] To overcome these drawbacks and to provide alternative molecules with improved film stability and morphology, like compound 2,[1,4] nitrogen-containing derivatives of pentacene, known as N-heteroacenes, have been investigated.[4–15] The synthesis of N-heteroacenes and the investigation of their properties has a long-standing history.[14] In 1901, Hinsberg published a comprehensive investigation of these ring systems discovering their chemical stability and fluorescence properties.[16] In the 1960s, Kummer and Zimmermann have systematically studied the electronic properties of linear diaza- and tetraazaacenes and compared these properties with that of the parent oligoacenes.[17] Nuckolls and co-workers have demonstrated the fabrication of a thin-film transistor based on a hydrogenated diazapentacene.[11] Winkler and Houk have discussed the application of nitrogen-containing oligoacenes as n-channel transistors based on density functional calculations.[14]

N-Heteroacenes are made from dihydrophenazine or dihydrodropyrazine units which add four electrons to the π system and stabilise the molecule. The presence of the hydrogen donor (dihydrophenazine N–H) and the hydrogen acceptor sites (phenazine N) leads to intermolecular hydrogen bonding networks forming a stable arrangement in the solid state.[19]

Large N-heteroacenes have been made by various methods. Phenazinediamine and its analogues have been used as building blocks,[20] three-dimensional pyrene-fused N-heteroacenes were made by an iterative approach,[21] layered thiadiazoloquinoxaline-containing long pyrene-fused N-heteroacenes,[22] azacacenodibenzosuberones,[23] N-heteroacenes extended through a four-membered ring,[24] N-phenylated N-heteroacenes,[25] and novel types of sulfur-nitrogen-containing N-heteroacenes containing a high proportion of heteroatoms.[26]

In the preliminary communication here, we report a synthesis and crystallographic structure for a non-planar mono-N substituted dihydrophenazine and explain its significance.

2. Results and Discussion

The starting materials for this study were commercially available (Figure 2). Compound 3 failed to give the desired product 8 by reaction with compound 6 (Figure 3). A reaction occurred but either side reactions happened or the product 8 was too insoluble and difficult to purify. Compound 4 reacted smoothly with compound 6, forming a green structure proposed as compound 7 in about 40% yield (Rf = 0.8 in DCM). Single crystals failed to give a diffraction pattern. Compound 5 failed...
to react with compound 6 in refluxing EtoH after 24 h to form compound 9, presumably because compound 5 is more sterically hindered and the expected product 9 is more puckered and strained than compound 7. Just the two starting materials were present by TLC of the reaction. Compound 7 is difficult to handle with poor stability, but out of phenazines 7–9 it is the easiest to make. In MeOH it is stable, but a dilute solution in DCM, in the dark or under irradiation with a 6 W lamp at 254 nm for 15 min, it decomposes or rearranges to a purple compound proposed as structure 15.

**Scheme 1.** Synthesis of compound 11 in low yield by nucleophilic displacement of a nitro group.

### 3. Crystal Structure of N-Butyl-5-methyl-3-nitro-5,10-dihydrophenazine 11

Compound 11 contains one molecule in the asymmetric unit (Figure 4). The dihydrophenazine ring system in compound 11 is slightly puckered with a dihedral angle of 4.90(8)° between the C1–C6 and C7–C8 benzene rings. The central heterocycle adopts a shallow boat conformation with N1 and N2 displaced by −0.049(3) and −0.095(3) Å from atoms C1/C6/C7/C8 (rms deviation = 0.005 Å). The N4/O1/O2 nitro group is almost coplanar with its attached aromatic ring [dihedral angle = 4.00(16)°] and this conformation is supported by an intramolecular N3–H3n–O1 hydrogen bond [H–O = 1.91(3) Å, N–H–O = 134(2)°], which closes an S(6) ring. The N-butyl side chain has an anti-gauche-anti conformation as shown by the following torsion angles: C10–N3–C14–C15 = 176.0(2)°; N3–C14–C15–C16 = −61.9(3)°; C14–C15–C16–C17 = −175.4(2)°. In the extended structure, N1–H1n O2 hydrogen bonds [H–O = 1.95(3) Å, N–H–O = 162(3)°] link the molecules into [010] C(8) chains, with adjacent molecules related by 2_{1} screw axis symmetry. Possible weak aromatic π–π stacking interactions between the heterocyclic rings [shortest centroid-centroid separation = 3.5775(12) Å] may help to consolidate the packing.

### 4. Conclusions

An advanced intermediate 11 for a potential iterative synthesis of 1,4-dihydro-N-heteroacenes has been characterised. A 1,4-disubstituted strip of 1,4-dihydro-N-heteroacenes or dihydrophenazines is expected to flex like a ruler when heated in solution, because of the dihydrophenazine butterfly shape and 30° angle between the rings, and ultimately be derivatised so as to condense and cyclise.
Experimental Section

IR spectra were recorded on an ATI Mattson Fourier transform infrared (FTIR) spectrometer using KBr discs. Ultraviolet (UV) spectra were recorded using a PerkinElmer Lambda 25 UV/Vis spectrometer with EtOH as the solvent. 1H and 13C nuclear magnetic resonance (NMR) spectra were recorded at 400 and 100 MHz, respectively, using a Varian 400 spectrometer. Chemical shifts, δ, are given in ppm and measured by comparison with the residual solvent. Copies of the NMR spectra and 13C nuclear magnetic resonance (13C NMR) spectra were recorded using a Varian 400 spectrometer. Chemical shifts, δ, are given in ppm and measured by comparison with the residual solvent.

Figure 4. The molecular structure of compound 11 showing 50% displacement ellipsoids.

N-Butyl-5-methyl-3-nitro-5,10-dihydrophenazine 11

Dinitrophenazine 7 (30 mg, 0.1 mmol) was treated with nBuNH2 (22 mg, 0.3 mmol, 3 eq) and Hünigs base (54 mg, 0.4 mmol) and refluxed in EtOH (40 ml) for 48 h. The mixture was evaporated to dryness and purified by chromatography on flash silica gel. The column was initially eluted with DCM to remove unreacted starting material (8 mg) followed by EtO/light petrol (50:50) and EtO to elute the title compound 11 (6 mg, 18%) as a red solid, mp. >200°C (from DCM) and a single spot by TLC (Rf=0.7 with eluent EtO). The structure was proven by a X-ray single-crystal structure determination.

Crystal Structure Determination of 11

C13H16N3O4 + H+ requires 313.1664.

10-Methyl-3-nitrophenazin-2-(10H)-one 10

Compound 7 (30 mg, 0.1 mmol) in DCM (100 ml) was irradiated in a quartz immersion well with a 6 W 254 nm lamp for 15 min. The solution turned from dark green to purple. The DCM was evaporated in vacuo and the product was purified by chromatography on silica gel. Elution with 20% aq. NH4OH eluted the title compound. 10 (12 mg, 47%) is a purple solid, mp. >200°C (from DCM) and a single spot by TLC (Rf=0.1 with eluent MeOH).

λmax (EtOH)/nm: 534 (log ε 2.8), 373(2.7) and 280 (3.2); νmax (diamond)/cm⁻¹: 3308(8), 1647(2), 1612(2), 1531(3), 1330(m), 1248(m), 1058(w), 1011(w), 893(2), 848(w), 815(s), 716(s), 653(w), 596(w), 573(w) and 555(w); δH (400 MHz; CDCl3)/ppm: 3.89 (3H, s), 6.38 (1H, s), 7.58 (1H, t, J=8.0 and 8.0 Hz), 7.66 (1H, d, J=8.0 Hz), 7.83 (1H, t, J=8.0 and 8.0 Hz), 8.07 (1H, d, and 8.13 (1H, d, J=8.0 Hz); δC (100.1 MHz; CDCl3)/ppm: 34.1, 100.7, 113.9, 125.3, 128.2, 132.2, 132.4, 136.7, 138.2, 145.1, 150.9 and 172.4; m/z (Orbitrap ASAP): 256.0728 [M+H]+, 100%, C9H9N3O4 + H+ requires 256.0722.
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Conflict of Interest

The authors declare no conflict of interest.

Keywords: N-heteroacenes · heterocycles · iterative synthesis · nucleophilic substitution · phenazines


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