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).[7,8] However, it suffers from long-term stability because of its photo-oxidation and low thermal stability.[9] To overcome these drawbacks and to provide alternative molecules with improved film stability and morphology, like compound 2,[10] nitrogen-containing derivatives of pentacene, known as N-heteroacenes, have been investigated.[11–13] 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.[15] 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.[16] Nuckolls and co-workers have demonstrated the fabrication of a thin-film transistor based on a hydrogenated diazapentacene.[17] Winkler and Houk have discussed the application of nitrogen-rich oligoacenes as n-channel transistors based on density functional calculations.[18]

N-Heteroacenes are made from dihydrophenazine or dihydrodropyrazine units which add four electrons to the r system and stabilise the molecule.[19] 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.[20]

Large N-heteroacenes have been made by various methods. Phenazinediamine and its analogues have been used as building blocks,[21] three-dimensional pyrene-fused N-heteroa-

cenes were made by an iterative approach,[22] layered thiadiazoloquinoxaline-containing long pyrene-fused N-heteroa-
cenes,[23] azaaacenodibenzosuberones,[24] N-heteroacenes extended through a four-membered ring,[25] N-phenylated N-
heteroacenes,[26] and novel types of sulfur-nitrogen-containing N-heteroacenes containing a high proportion of heteroatoms.[27]

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 10. 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 10. Its structure was solved by an X-ray single-crystal structure determination with correct accurate mass. Luckily for these studies, the nitro groups of 1,2-dinitrobenzene are labile to amine nucleophiles,[27] and treatment of the intermediate 7 with butylamine in hot EtOH with Hünig’s base gave compound 11 as pure red crystals in a low yield of 18% and low conversion (Scheme 1). Improvement of the yield was not achieved by doing the reaction in a digestion bomb at 150 °C, using a 20-fold excess of butylamine in refluxing EtOH or neat butylamine at rt. Its structure was solved by an X-ray single-crystal structure determination with good data. This product proves the structure of the precursor 7. It is not immediately obvious why only one of the nitro groups is selectively displaced, although this is desirable. The low yield of this reaction is disappointing as is the stability of compound 7, which are impediments to an iterative synthesis. Reduction of the nitro group in compound 11 would generate a new monoalkyl-phenylendiamine 12 so the cycle can be repeated, generating an array. Dihydrophenazines are not planar, but are puckered or butterfly-shaped,[28] so a strip is expected to flex like a ruler when heated and ultimately condense and cyclise.

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 2,2-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.

![Scheme 1. Synthesis of compound 11 in low yield by nucleophilic displacement of a nitro group.](Image)
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. IR spectra were recorded on an ATI Mattson Fourier transform infrared (FTIR) spectrometer using KBr discs. Ultraviolet (UV) spectra were recorded using a Varian 400 spectrometer. Chemical shifts, δ, are given in ppm and measured by comparison with the residual solvent. Coupling constants, J, are given in Hz. Copies of the NMR spectra are provided in the Supporting Information. High-resolution mass spectra were obtained at the University of Wales, Swansea, using an Atmospheric Solids Analysis Probe (ASAP) (Positive mode) Instrument: Xevo G2-S ASAP. Melting points were determined on a Kofler hot stage microscope. The starting materials were purchased from Sigma-Aldrich and compound 6 from Fluorochem. The purity of new compounds was ascertained by Thin Layer Chromatography (TLC) on alumina-backed TLC plates.

5-Methyl-2,3-dinitro-5,10-dihydrophenazine 7

N-Methyl-o-phenylenediamine 4 (300 mg, 2.5 mmol) and 4,5-difluoro-1,2-dinitrobenezene 6 (500 mg, 2.5 mmol) were refluxed in EtOH (40 ml) with EtOCl (40 ml) with EtOCl (40 ml) with EtOCl (40 ml) with EtOCl (40 ml). The column was initially eluted with DCM to remove unreacted starting material (8 mg) followed by EtOCl/light petrol (50:50) and EtOCl 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 EtOCl). The structure was proven by an X-ray single-crystal structure determination.

Crystal Structure Determination of 11

C18H16N4O4, Mw = 312.37 g mol⁻¹, dark red plate, 0.18 × 0.08 × 0.01 mm, Rigaku CCD diffractometer, CuKα radiation (λ = 1.54184 Å), T = 100 K, monoclinic, P2₁/c, α = 14.7861(3) Å, b = 15.3750(3) Å, c = 8.960(4) Å, β = 93.408(2)°, V = 1579.67(6) Å³, Z = 4, 14854 reflections with 2θ < 151.5°, R = 0.048, 216 parameters, R(F) [2701 reflections with I > 2σ(I)] = 0.066, wR(F²) [3181 reflections] = 0.155. The N-bound H atoms were located in difference maps and freely refined; the C-bound H atoms were refined as riding atoms in idealised locations (full details in deposited CIF file).

Deposition Number 2088092 (for 11) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.
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Conflict of Interest

The authors declare no conflict of interest.

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