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,[1–5] optical properties[6–9] and device physics (Figure 1).[10,11] 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**,[13] nitrogen-containing derivatives of pentacene, known as N-heteroacenes, have been investigated.[14–15] The synthesis of N-heteroacenes and the investigation of their properties has a long-standing history.[15] 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.[13] Winkler and Houk have discussed the application of nitrogen-rich oligoacenes as n-channel transistors based on density functional calculations.[14]

N-Heteroacenes are made from dihydrophenazine or dihydropyrazine units which add four electrons to the π system and stabilise the molecule.[18] Secondly, 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] azaacenodibenzosuberones,[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]

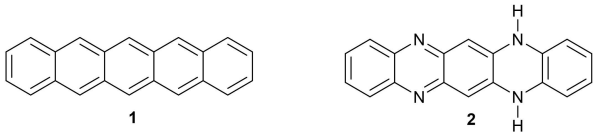

Figure 1. A comparison of pentacene with an N-heteroacene.

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 ($R_f = 0.8$ in DCM). Single crystals failed to give a diffraction pattern. Compound **5** failed

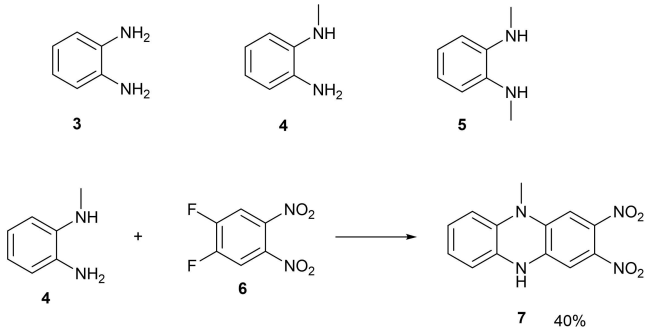

Figure 2. The reaction of *o*-phenylenediamines **3**–**5** was studied with 4,5-difluoro-1,2-dinitrobenzene **6**.

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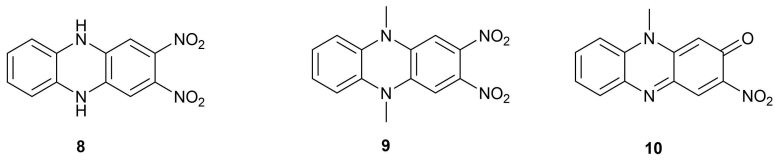


Figure 3. Phenazines 8–10.

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 **10**. This structure fits the spectroscopic data and it has a long wavelength absorption at 534 nm, an IR absorption at 1670 cm^{-1}, a carbonyl group ^{13}C NMR peak at 172.4 ppm and a molecular ion of 255 with the 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-*o*-phenylenediamine **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.

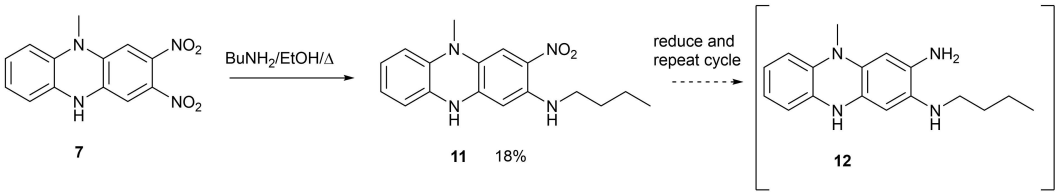
3. Crystal Structure of *N*-Butyl-5-methyl-3-nitro-5,10-dihydrophenazine 11

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_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.



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

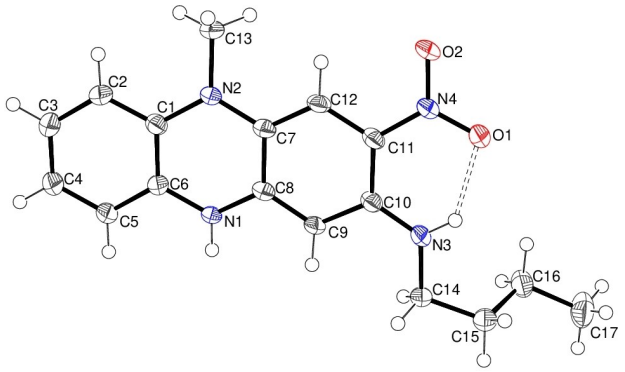


Figure 4. The molecular structure of compound **11** showing 50% displacement ellipsoids.

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. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded at 400 and 100.5 MHz, respectively, 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 **3**–**5** 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-dinitrobenzene **6** (500 mg, 2.5 mmol) were refluxed in EtOH (40 ml) with Et_3N (496 mg, 5.0 mmol) for 24 h. After cooling, the reaction was either evaporated to dryness or diluted with dilute aq. HCl (100 ml) (1.0 M) and extracted with DCM (2x 50 ml), then evaporated. In either case, the residue was applied to a flash silica column (12 inches long) and the mixture eluted with DCM. The product is very dark and is easily collected. Typically, the dark bands of by-products are left behind on the column before being eluted, so banding is seen at the front and back of the product band. Smaller scales of the reaction may be easier to avoid overloading the column. The title compound **7** (259 mg, 37%) is a dark solid, mp. 150–151 °C (from DCM) and a single spot by TLC (R_f = 0.8 with eluent DCM). The crystals did not diffract when investigated by an X-ray single-crystal structure determination).

λ_{max} (EtOH)/nm: 549 (log ε 3.3), 433 (3.4) and 309 (4.0); $\bar{\nu}_{max}$ (diamond)/cm^{-1}: 3289(w), 1637(w), 1610(w), 1532(s), 1495(s), 1358 (s), 1270(s), 1218(s), 1066(s), 851(m), 815(m), 736(s) and 598(m); δ_H (400 MHz; DMF-d_7)/ppm: 2.98 (3H, s), 6.29 (1H, d, *J* = 8.0 Hz), 6.50 (1H, d, *J* = 8.0 Hz), 6.55 (1H, s), 6.59 (1H, t, *J* = 8.0 and 8.0 Hz), 6.64 (1H, t, *J* = 8.0 and 8.0 Hz), 6.69 (1H, s) and 8.99 (1H, s); δ_C (100.1 MHz; DMF-d_7)/ppm: 31.8, 104.5, 105.4, 112.8, 113.1, 123.2, 123.2, 133.2, 133.7, 136.7, 138.0, 140.3 and 141.9; *m/z* (Orbitrap ASAP): 287.0779 ($[M+H]^+$, 100%), $C_{13}H_{10}N_4O_4+H^+$ requires 287.0780.

10-Methyl-3-nitrophenazin-2-(10*H*)-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 had 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. NH_3/MeOH eluted the title compound. **10** (12 mg, 47%) is a purple solid, mp. > 200 °C (from DCM) and a single spot by TLC (R_f = 0.1 with eluent MeOH).

λ_{max} (EtOH)/nm: 534 (log ε 2.8), 373(2.7) and 280 (3.2); $\bar{\nu}_{max}$ (diamond)/cm^{-1}: 3308(w), 1647(w), 1612(w), 1531(s), 1330(m), 1248 (m), 1058(w), 1011(w), 893(w), 848(w), 815(s), 716(s), 653(w), 596(w), 573(w) and 555(w); δ_H (400 MHz; $CDCl_3$)/pmm: 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), 7.86 (1H, t, *J* = 8.0 and 8.0 Hz), 8.07 (1H, s) and 8.13 (1H, d, *J* = 8.0 Hz); δ_C (100.1 MHz; $CDCl_3$)/ppm: 34.1, 100.7, 113.9, 125.3, 128.2, 132.2, 132.4, 135.1, 136.7, 138.2, 145.1, 150.9 and 172.4; *m/z* (Orbitrap ASAP): 256.0728 ($[M+H]^+$, 100%), $C_{13}H_9N_3O_3+H^+$ requires 256.0722.

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

Dinitrophenazine **7** (30 mg, 0.1 mmol) was treated with *n*$BuNH_2$ (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 Et_2O/light petrol (50:50) and Et_2O to elute the title compound **11** (6 mg, 18%) as a red solid, mp. > 200 °C (from DCM) and a single spot by TLC (R_f = 0.7 with eluent Et_2O). The structure was proven by an X-ray single-crystal structure determination.

λ_{max} (EtOH)/nm 569 (log ε 3.5), 424 (3.2) and 316 (3.6); (diamond)/cm^{-1}: 2935(w), 2927(w), 1634(w), 1607(w), 1486(s), 1285(s), 1084(m), 820(m), 738(s) and 584(w); δ_H (400 MHz; $CDCl_3$)/ppm: 0.91 (3H, t, *J* = 8.0 Hz), 1.37–1.67 (4H, m), 3.20 (3H, s), 3.27 (2H, q, *J* = 8.0 Hz), 6.07–6.23 (1H, s, br), 6.26 (1H, s), 6.46–6.54 (1H, s, br), 7.38 (1H, t, *J* = 8.0 and 8.0 Hz), 7.48 (1H, t, *J* = 8.0 and 8.0 Hz), 7.52 (1H, s), 7.54 (1H, d, *J* = 8.0 Hz) and 7.92 (1H, d, *J* = 8.0 Hz); δ_C (100.1 MHz; $CDCl_3$)/ppm: 13.7, 20.4, 29.5, 30.5 (Bu), 42.5 (NCH_3), 96.8, 113.6, 118.3, 124.7, 128.4 and 129.1 (6×CH); *m/z* (Orbitrap ASAP): 313.1668 ($[M+H]^+$, 100%), $C_{17}H_{20}N_4O_2+H^+$ requires 313.1664.

Crystal Structure Determination of 11

$C_{17}H_{20}N_4O_2$, M_r = 312.37 g mol^{-1}, dark red plate, 0.18 × 0.08 × 0.01 mm, Rigaku CCD diffractometer, $Cu_{K\alpha}$ radiation (λ = 1.54184 Å), *T* = 100 K, monoclinic, $P2_1/c$, *a* = 14.7861(3) Å, *b* = 15.3750(3) Å, *c* = 6.9609(2) Å, β = 93.408(2)°, *V* = 1579.67(6) $Å^3$, *Z* = 4, 14854 reflections with $2\theta < 151.5°$, R_{int} = 0.048, 216 parameters, *R*(*F*) [2701 reflections with $I > 2\sigma(I)$] = 0.066, *wR*(F^2) (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.

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

[1] J. L. Bredas, J. P. Calbert, D. A. da Silva Filho, J. Cornil, *Org. Semi. Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 5804–5809.
[2] Y. C. Cheng, R. J. Silbey, D. A. da Silva Filho, J. P. Calbert, J. Cornil, J. L. Bredas, *J. Chem. Phys.* **2003**, *118*, 3764.
[3] K. Hummer, C. Ambrosch-Draxl, *Phys. Rev. B: Condens. Matter Mater. Phys.* **2005**, *72*, 205205.
[4] D. Nabok, P. Puschnig, C. Ambrosch-Draxl, O. Werzer, R. Resel, D.-M. Smilgies, *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, *76*, 235322.
[5] S. Sharifzadeh, A. Biller, L. Kronik, J. B. Neaton, *Phys. Rev. B: Condens. Matter Mater. Phys.* **2012**, *85*, 125307.
[6] M. L. Tiago, J. E. Northrup, S. G. Louie, *Phys. Rev. B: Condens. Matter Mater. Phys.* **2003**, *67*, 115212.
[7] K. Hummer, C. Ambrosch-Draxl, *Phys. Rev. B: Condens. Matter Mater. Phys.* **2005**, *71*, No. 081202(R).
[8] C. Ambrosch-Draxl, D. Nabok, P. Puschnig, C. Meisenbichler, *New J. Phys.* **2009**, *11*, 125010.
[9] T. Rangel, K. Berland, S. Sharifzadeh, F. Brown-Altvater, K. Lee, P. Hyldgaard, L. Kronik, J. B. Neaton, *Phys. Rev. B* **2016**, *93*, 115206.
[10] H. Klauk, U. Zschieschang, J. Pflaum, M. Halik, *Nature* **2007**, *445*, 745–748.
[11] M. Kitamura, Y. Arakawa, *J. Phys. Condens. Matter* **2008**, *20*, 184011.
[12] A. Maliakal, K. Raghavachari, H. Katz, E. Chandross, T. Siegrist, *Thin Films* **2004**, *16*, 4980–4986.
[13] B. Kollmann, Z. Chen, D. Lüftner, O. Siri, P. Puschnig, *J. Phys. Chem. C* **2018**, *122*, 6475–6482.
[14] Q. Miao, T.-Q. Nguyen, T. Someya, G. B. Blanchet, C. Nuckolls, *J. Am. Chem. Soc.* **2003**, *125*, 10284–10287.
[15] U. H. F. Bunz, *Pure Appl. Chem.* **2010**, *82*, 953–968.
[16] O. Hinsberg, *Liebigs Ann. Chem.* **1901**, *319*, 257–286.
[17] F. Kummer, H. Zimmermann, *Phys. Chem.* **1967**, *71*, 1119–1126.
[18] J. I. Wu, C. S. Wannere, Y. Mo, P. v. R Schleyer, U. H. F. Bunz, *J. Org. Chem.* **2009**, *74*, 4343–4349.
[19] T. Lelaidier, T. Leoni, P. Arumugam, A. Ranguis, C. Becker, O. Siri, *Langmuir* **2014**, *30*, 5700–5704.
[20] J. Li, Y. Shen, J. Wan, X. Yu, Q. Zhang, *Eur. J. Org. Chem.* **2018**, 3375–3390.
[21] B.-L. Hu, C. An, M. Wagner, G. Ivanova, A. Ivanova, M. Baumgarten, *J. Am. Chem. Soc.* **2019**, *141*, 5130–5134.
[22] B.-L. Hu, K. Zhang, C. An, D. Schollmeyer, W. Pisula, M. Baumgarten, *Angew. Chem. Int. Ed. Engl.* **2018**, *57*, 12375–12379.
[23] V. Brosius, M. Müller, J. Borstelmann, F. Rominger, J. Freudenberg, U. H. F. Bunz, *J. Org. Chem.* **2020**, *85*, 296–300.
[24] S. J. Yang, B. W. Shan, X. M. Xu, Q. Miao, *Chem. Eur. J.* **2016**, *22*, 6637–6642.
[25] X. Gu, B. Shan, Z. He, *ChemPlusChem* **2017**, *82*,1034–1038.
[26] H.-S. Guo, M.-F. Liu, Y. Han, S. Han, Y.-L. Chen, *Chin. J. Polym. Sci.* **2016**, *34*, 1319–1329.
[27] S. M. Chiacchiera, J. O. Singh, J. D. Anunziata, J. J. Silber, *J. Chem. Soc.-Perkin Trans.* **1988**, *11*, 1585–1589.
[28] M. Holzapfel, C. Lambert, C. Selinka, D. Stalke, *J. Chem. Soc. Perkin Trans. 2* **2002**, 1553–1561.

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