Potential Building Blocks for 1,4-Dihydro-\(\text{N}\)-heteroacenes

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Studies have been performed aimed at the synthesis of \(\text{N}\)-heteroacenes via substitution reactions of 4,5-difluoro-1,2-dinitrobenzene with a diamine. The fluorine atoms are displaced first, followed by an activated nitro group. Two intermediates have been characterised by X-ray single-crystal structure determinations. Their intermolecular interactions were examined by Hirshfeld surfaces to assess their suitability for organic molecular electronics. The high reactivity of the phenazine, which is prone to oxidise and rearrange, as are displacement products prepared from it, is explained by the formation of a cis-aci-nitro form from the secondary amine of the phenazine and a nitro group.

Introduction

\(\text{N}\)-Heteroacenes are of interest for their electronic,[1–3] sensing[4] and fluorescent[5] properties and they have been considered as nanocarbon segments,[6] for two-photon absorption[7] and for photovoltaics.[8] Progress has also been made in the synthesis of \(\text{S,N}\)-heteroacenes which are novel types of sulfur-nitrogen containing heteroacenes which have a high proportion of heteroatoms.[9–11] Large \(\text{N}\)-heteroacenes have been made by various methods. Phenazine and its analogues have been used as building blocks[12] and three-dimensional pyrene-fused \(\text{N}\)-heteroacenes were made by an iterative approach.[13] \(\text{N}\)-Heteroacenes have been extended through a four-membered ring[14] and \(\text{N}\)-phenylated \(\text{N}\)-heteroacenes are known.[15] Layered thiadiazoloquinoline containing long pyrene-fused \(\text{N}\)-heteroacenes[16] and azaacenodibenzosuberones.[17] Acenes containing heteroatoms have been solubilised with different side chains and can be doped making them of interest in optoelectronics and organic electronic devices.[18] The \(\text{N}\)-heteroacene framework allows for more versatile synthetic routes for its construction, compared to acenes, with condensations using substituted \(\text{o}\)-phenylenediamines, benzothiadiazoles and pyrene quinones.[19] Synthetic control of the conjugated heterocycle length is possible adjusting the properties for organic solar cells.[19–20] Organic field effect transistors[21–22] and organic light emitting diodes.[23–24] \(\text{N}\)-Heteroacenes are also under study as a new generation of Organic Resistance Memory (ORM) devices which have potential as an information storage technology to replace inorganic silica based memories.[25–27]

However their current properties are unsuitable compared to modern transistors and their improvement poses a research challenge with modern materials.[28] \(\text{N}\)-Heteroacenes capped at both ends with thiadiazoles have been studied which increases the device efficiency.[29] A simple route to unsubstituted \(\text{N}\)-heteroacenes has been reported by the condensation of 1,2,4,5-tetraaminobenzene with 1,10-phenanthrolene-5,6-dione.[30] Tetraazapentacene and tetraazaheptacene derivatives were prepared solubilised with ethyl-\(\text{N}\)-trisopropylsilyle groups. They were capped with phenanthrenes at each end to stabilise them.[30] Dimers and trimers of phenylene bridged cyclic azacenes can be prepared by multiple benzo diamine condensations or by Buchwald-Hartwig-type palladium-catalysed couplings.[31]

A computational comparison of the properties of dihydrottetraazapentacenes and their derivatives with those of acenes has been made.[32] They are predicted to be more stable than the corresponding acenes. A twin donor composed of cofacially stacked dihydrodiazapentacenes has been studied experimentally and computationally which shows an expected but partial butterfly shape.[33–34] The aromatic stability of \(\text{N}\)-heteroacenes might be probed by P. Schleyers work on acenes[35] and Nucleus-Independent Chemical Shifts (NICS)[36] which could help in the design of new, stable materials. Novel methodologies also exist that might be developed such as R. Beckert’s synthesis of fluorubine[37] and the synthesis by G. J. Richards and J. P. Hill of fluorescent pyrazacenes.[38]

Results and Discussion

We recently reported groundwork for a potential iterative approach to prepare \(\text{N}\)-heteroacenes (Scheme 1).[39] 1,2-Difluoro-4,5-dinitrobenzene 2 has dual-mode or ambident reactivity. The fluorine atoms are firstly displaced by diamine 1, forming \(\text{N}\)-methylphenazine 3 and a nitro group is displaced[40] next by butylamine forming compound 4. Reduction of the nitro group would regenerate an \(\text{N}\)-butyl-\(\text{o}\)-phenylenediamine intermediate 5 that could repeat the cycle by reacting with compound 2. However, the intermediates we prepared had poor thermal and oxidative stability and were not best suited for an iterative synthesis. This paper reports further groundwork aimed at an iterative approach to making \(\text{N}\)-...
heteroacenes and an understanding of the intermediate chemistry.

After preparing small batches of 2-(butylamino)-5-methyl-3-nitro-5,10-dihydrophenazine \( \text{4}^{[39]} \) a number of times we noticed a more polar red product on the flash silica column (Figure 2). This was only observed when old batches of the starting material, kept in the dark in a sealed sample vial for about eight weeks, were used. This new compound was purified by gradient elution column chromatography and fully characterised including an X-ray single-crystal structure determination. Scheme 2 shows a drawing of the structure, compound \( \text{6} \), and Figure 1 shows the molecular structure from the crystallographic characterisation. The parent compound of heterocycle \( \text{6} \) has been prepared by synthesis\(^{[41]} \) and oxidation.\(^{[42]} \)

The crystal structure of compound \( \text{6} \) indicates that the entire molecule is close to planar (r.m.s. deviation for 24 non-hydrogen atoms = 0.077 Å). A more detailed analysis shows that the phenazine ring system is slightly puckered with a statisti-
The minor pathway leads to compound 8. These dyes are more stable than the starting material 3 and suggest that iterative 1,4-dihydro-N-heteroacene synthesis may require more hindered structures or N-1,4-disubstituted structures.

In compound 8, the phenazine ring system is close to planar (r.m.s. deviation for C1–C13/N1/N2/O1 = 0.041 Å) as expected but a more detailed analysis shows a slight pucker as indicated by the dihedral angle of 2.3(4)° between the C1–C6 and C7–C12 benzene rings: the central heterocycle is statistically planar, although the geometrical precision is low. Unlike the situation in compound 6, the N3/O2/O3 nitro group in compound 8 is substantially twisted away from its attached benzene ring by 55.7(3)°, presumably due to steric crowding with the adjacent C1–O1 group. The C1–O1, C2–C3 and C4–N2 bond lengths are 1.236(9), 1.314(11) and 1.318(10) Å, respectively. As noted above for compound 6, this C=O bond length...
of 1.24 Å is slightly longer than an ‘isolated’ C–O double bond of 1.20 Å, suggesting a degree of intramolecular charge transfer from N1. In the extended structure of compound 8, weak C–H–O and C–H–N interactions help to establish the packing. The IR stretch of the C=O bond was also low at 1647 cm⁻¹ owing to conjugation. For compound 8 (λmax = 534 nm), the HOMO-LUMO gap or ΔE = NhC/λ = 223 kJ mol⁻¹ owing to conjugation from N1 to the C–O bond and the nitro group.

The Hirshfeld surface of compound 8 (Figure 4) shows a number of intense red spots in the vicinities of the H atoms (donors) and O and N atoms (acceptors) associated with the intermolecular C–H–O and C–H–N interactions. The major fingerprint percentages are H–O/O–H (34.5 %), H–H (24.8 %) and C–C (11.8 %).

The next step was to show that 10-methyl-7,8-dinitrophenazin-2(10H)-one 7 undergoes nucleophilic substitution with butylamine to give compound 6 (Scheme 4). This is the case and as expected only one of the nitro groups is displaced in a clean and high yielding reaction. The starting material 7 and product 6 have similar Rf values. A TLC plate eluted with Et₂O/MeOH (99.5:0.5) distinguished the brighter red compound from the less polar red starting material (Rf = 0.2). The nitro group at the 8-position is activated by both the carbonyl group and a nitro group. Nucleophilic attack at this position can delocalise the negative charge of the anionic intermediate onto the carbonyl group. This is not the case for the nitro group at the 7-position which is less reactive overall.

By chance it was observed that a purple solution of compound 4 in xylene rapidly changed to a yellow solution after a few minutes (Scheme 5). The product, compound 9, was fully characterised by spectroscopic methods. A non-polar solvent favoured this rearrangement or oxidation. Since compounds 3 and 4 are stable in ethanol under reflux for 24–48 h without precautions to exclude air or oxygen, this suggests a spontaneous rearrangement occurs to a stable product. The solubility of oxygen in xylene is also similar to that in ethanol.

One possibility might involve a type of cis-aci-nitro fragmenting (Scheme 6).

Conclusion

A new product has been isolated from the reaction of butylamine with 5-methyl-2,3-dinitro-5,10-dihydrophenazine 3 that had been stored in the dark for eight weeks in a sealed sample vial. The structure of this product, 8-(butylamino)-10-methyl-7-nitrophenazin-2(10H)-one 6, was proven by an X-ray single-crystal structure determination and spectroscopic characterisation. Subsequently, the starting material was analysed and was found to be decomposing into two compounds, 10-methyl-
7,8-dinitrophenazin-2(10H)-one 7 and 10-methyl-3-nitrophenazin-2(10H)-one 8.\(^{35}\) To verify the pathway for the formation of compound 6, compound 7 was treated with butylamine which gave compound 6 in a high yielding and clean reaction. Further verification of the decomposition pathway was provided by the spontaneous rearrangement of 2-(butylamino)-5-methyl-3-nitro-5,10-dihydrophenazine 4 to 3-(butylamino)-10-methylphenazin-2(10H)-one 9 in xylene at room temperature in a few minutes. Hirshfeld surfaces indicate points of close contact in molecules 6 and 8 which have potential for electron transfer and they are likely to be harder to make. Substituted 1,4-dihydropyrazines are more puckered,\(^{36}\) so are likely to be harder to make.

**Experimental Section**

IR spectra were recorded on a diamond Attenuated Total Reflection (ATR) Fourier transform infrared (FTIR) spectrometer. Ultraviolet (UV) spectra were recorded using a PerkinElmer Lambda 25 UV-Vis spectrometer with ETOH as the solvent. The term sh means shoulder. \(^1\)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, \(\delta\), are given in ppm and measured by comparison with the residual solvent. Coupling constants, \(J\), are given in Hz. 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.

8-(Butylamino)-10-methyl-7-nitrophenazin-2(10H)-one 6

A batch of 5-methyl-2,3-dinitro-5,10-dihydrophenazine 3 that was over 8 weeks old and had been stored in a sealed vial (15 mg, 0.052 mmol) was purified by chromatography on silica gel. CHCl\(_3\) eluted the starting material (10 mg, 67%), then CH\(_2\)Cl\(_2\)/MeOH (10:90) eluted the title compound 7 (1 mg, 6%), then 10-methyl-3-nitrophenazin-2(10H)-one\(^{16}\) 8 (4 mg, 30%), mp: >200 °C (from dichloromethane/petroleum ether).

**8-(Butylamino)-10-methyl-7-nitrophenazin-2(10H)-one 6**

IR (ATR Diamond)(cm\(^{-1}\)): 3353(w), 2959(w), 2931(w), 2864(w), 1601(s), 1541(s), 1442(m), 1339(m), 1254(s), 1234(s), 1193(s), 1058(m), 874(m), 839(m), 749(m), 528(s), 50 6(s), 462(m), 435(s)cm\(^{-1}\); UV/Vis (EOH): \(\lambda_{\text{max}}(\epsilon) = 534\text{sh}(10,000), 509\text{nm}(12,610), 413\text{sh}(2,520), 339\text{sh}(7,900), 248\text{nm}(10,000\text{ mol}^{-1}\text{ dm}^{-3}\text{ cm}^{-1})\); HRMS (ASAP Orbitrap) m/z calculated for C\(_{17}\)H\(_{14}\)N\(_3\)O\(_5\)+H\(^+\): 327.1452; found: 327.1452 (100%).

10-Methyl-7,8-dinitrophenazin-2(10H)-one 7

A batch of 5-methyl-2,3-dinitro-5,10-dihydrophenazine 3 that was over 8 weeks old and had been stored in a sealed vial (15 mg, 0.052 mmol) was purified by chromatography on silica gel. CHCl\(_3\) eluted the starting material (10 mg, 67%), then CH\(_2\)Cl\(_2)/MeOH (10:90) eluted the title compound 7 (1 mg, 6%), then 10-methyl-3-nitrophenazin-2(10H)-one\(^{16}\) 8 (4 mg, 30%), mp: >200 °C (from dichloromethane/petroleum ether).

**10-Methyl-7,8-dinitrophenazin-2(10H)-one 7**

IR (ATR Diamond)(cm\(^{-1}\)): 3353(w), 2959(w), 2931(w), 2864(w), 1601(s), 1541(s), 1442(m), 1339(m), 1254(s), 1234(s), 1193(s), 1058(m), 874(m), 839(m), 749(m), 528(s), 50 6(s), 462(m), 435(s)cm\(^{-1}\); UV/Vis (EOH): \(\lambda_{\text{max}}(\epsilon) = 534\text{sh}(10,000), 509\text{nm}(12,610), 413\text{sh}(2,520), 339\text{sh}(7,900), 248\text{nm}(10,000\text{ mol}^{-1}\text{ dm}^{-3}\text{ cm}^{-1})\); HRMS (ASAP Orbitrap) m/z calculated for C\(_{17}\)H\(_{14}\)N\(_3\)O\(_5\)+H\(^+\): 327.1452; found: 327.1452 (100%).

**3-(Butylamino)-10-methylphenazin-2(10H)-one 9**

IR (ATR Diamond)(cm\(^{-1}\)): 3353(w), 2959(w), 2931(w), 2864(w), 1601(s), 1541(s), 1442(m), 1339(m), 1254(s), 1234(s), 1193(s), 1058(m), 874(m), 839(m), 749(m), 528(s), 50 6(s), 462(m), 435(s)cm\(^{-1}\); UV/Vis (EOH): \(\lambda_{\text{max}}(\epsilon) = 534\text{sh}(10,000), 509\text{nm}(12,610), 413\text{sh}(2,520), 339\text{sh}(7,900), 248\text{nm}(10,000\text{ mol}^{-1}\text{ dm}^{-3}\text{ cm}^{-1})\); HRMS (ASAP Orbitrap) m/z calculated for C\(_{17}\)H\(_{14}\)N\(_3\)O\(_5\)+H\(^+\): 327.1452; found: 327.1452 (100%).
the xylene. Elution with MeOH/Et₂O (10:90) gave the title compound 9 (mp 32%, mp: > 200 °C (from dichlormethane: light petroleum ether).

1H NMR (400 MHz, D₂DMF, 25°C) 1.15 (3H, t, J = 8.0), 1.63 (2H, m), 1.90 (2H, m), 3.56 (2H, t, J = 8.0), 4.19 (3H, s), 6.47 (1H, s), 6.58 (1H, s), 6.79-6.86 (1H, s), 7.66 (1H, t, J = 8.0 and 8.0), 7.79 (1H, t, J = 8.0 and 8.0), 8.07 (1H, d, J = 8.0) and 8.13 (1H, d, J = 8.0); 13C NMR (100.1 MHz, D₂DMF, 25°C) 13.3, 20.2, 30.5, 33.8, 42.0, 166.3, 167.0, 114.7, 123.9, 128.2, 128.7, 129.4, 136.6, 136.9, 147.1, 148.3 and 176.4 Å;

SHELXT structures were routinely solved by dual-space methods using space group P2₁/c, radiation, λ = 1.54179 Å) at 100 K. The crystallographers were placed geometrically (C, 133.2, 20.2, 30.5, 33.8, 42.0, 166.3, 167.0, 114.7, 123.9, 128.2, 128.7, 129.4, 136.6, 136.9, 147.1, 148.3 and 176.4 Å; HRMS (ASAP Orbitrap) m/z calcld for C₁₁H₁₃N₃O₇H: 282.1601; found: 282.1603 (100%).

The proton and carbon NMR data for all compounds in the experimental section is reported in the Supporting Information as well as the proton NMR data for compound 3.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: 4,5-difluoro-1,2-dinitrobenzene - N-heterocenes - iterative synthesis - N-methyl-o-phenylenediamine

Supplemental Material

Deposition Numbers 2166565 (for 6) and 216658 (for 8) contain 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.

The proton and carbon NMR data for all compounds in the experimental section is reported in the Supporting Information as well as the proton NMR data for compound 3.

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