Research Article
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Potential Building Blocks for 1,4-Dihydro-*N*-heteroacenes

M. John Plater* and William T. A. Harrison[a]

Studies have been performed aimed at the synthesis of *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

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 S,N-heteroacenes which are novel types of sulfur-nitrogen containing heteroacenes which have a high proportion of heteroatoms.[9–11] Large *N*-heteroacenes have been made by various methods. Phenazinediamine and its analogues have been used as building blocks[12] and three-dimensional pyrene-fused *N*-heteroacenes were made by an iterative approach.[13] *N*-Heteroacenes have been extended through a four-membered ring[14] and *N*-phenylated *N*-heteroacenes are known.[15] Layered thiadiazoloquinoxaline containing long pyrene-fused *N*-heteroacenes[16] and azaacenodibenzosuberones.[1] Acenes containing heteroatoms have been solubilised with different side chains and can be doped making them of interest in optoelectronics and organic electronic devices.[17] The *N*-heteroacene framework allows for more versatile synthetic routes for its construction, compared to acenes, with condensations using substituted *o*-phenylenediamines, benzothiadiazoles and pyrene quinones.[17] Synthetic control of the conjugated heterocycle length is possible adjusting the properties for organic solar cells,[18–20] organic field effect transistors[21–22] and organic light emmitting diodes.[23–24] *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] *N*-Heteroacenes capped at both ends with thiadiazoles have been studied which increases the device efficiency.[8] A simple route to unsubstituted *N*-heteroacenes has been reported by the condensation of 1,2,4,5-tetraaminobenzene with 1,10-phenanthroline-5,6-dione.[29] Tetraazapentacene and tetraazaheptacene derivatives were prepared solubilised with ethnyltriisopropylsilyl groups. They were capped with phenanthrenes at each end to stabilise them.[30] Dimers and trimers of phenylene bridged cyclic azaacenes can be prepared by multiple benzoin diamine condensations or by Buchwald-Hartwig-type palladium-catalysed couplings.[31]

A computational comparison of the properties of dihydrotetraazapentacenes 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 *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 pyrazinacenes.[38]

Results and Discussion

We recently reported groundwork for a potential iterative approach to prepare *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 *N*-methylphenazine **3** and a nitro group is displaced[40] next by butylamine forming compound **4**. Reduction of the nitro group would regenerate an *N*-butyl-*ortho*-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 *N*-

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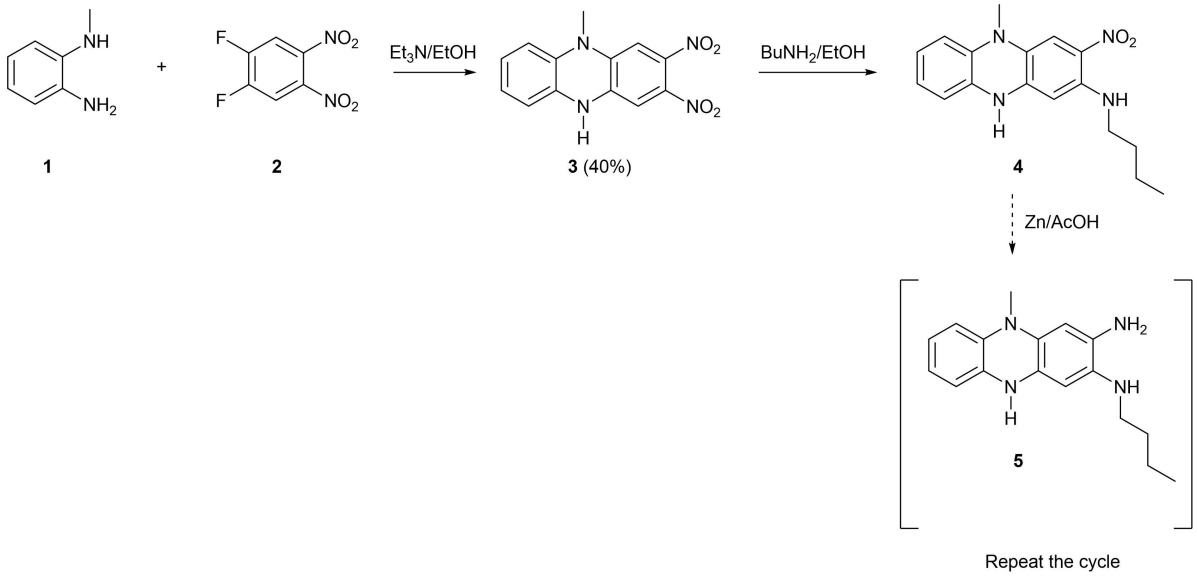
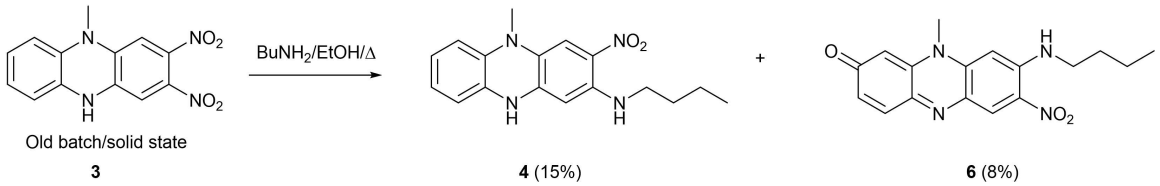


Scheme 1. Previously reported groundwork for an iterative N-heteroacene synthesis.[39]



Scheme 2. The reaction of an eight-week-old batch of compound **3** with *n*-butylamine.

heteroacenes and an understanding of the intermediate chemistry.

After preparing small batches of 2-(butylamino)-5-methyl-3-nitro-5,10-dihydrophenazine **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 **6**, and Figure 1 shows the molecular structure from the crystallographic characterisation. The parent compound of heterocycle **6** has been prepared by synthesis[41] and oxidation.[42]

The crystal structure of compound **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-

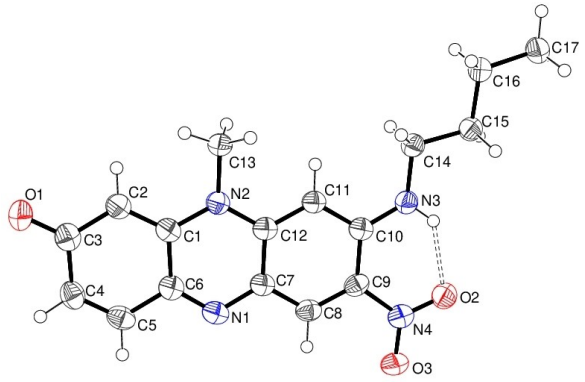


Figure 1. The molecular structure of compound **6** showing 50% displacement ellipsoids. The intramolecular N–H···O hydrogen bond is indicated by a double-dashed line.

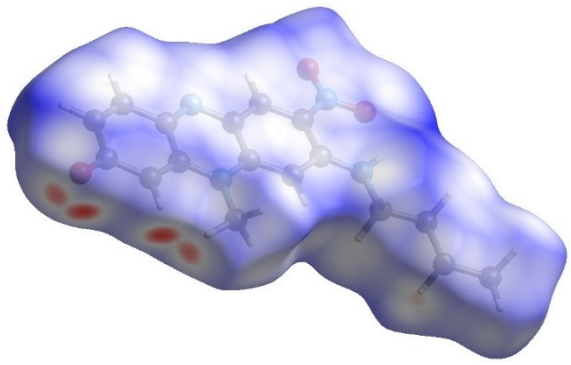
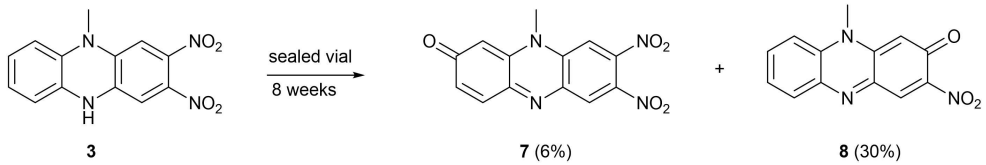


Figure 2. The Hirshfeld surface for compound **6** plotted over d_{norm} (−0.24 to 1.41 a.u.) showing red spots in the vicinities of atoms C2, C13 and O1, corresponding to directional intermolecular contacts.



3 7 (6%) 8 (30%)

Scheme 3. The solid state oxidation or rearrangement of compound **3** in a sealed sample vial at room temperature.

cally significant dihedral angle of 1.70(9)° between the C1–C6 and C7–C12 benzene rings. The central heterocycle is almost planar (r.m.s. deviation = 0.011 Å) but could alternately be described as a very shallow envelope with N2 displaced by −0.036(3) Å from the other five atoms (r.m.s. deviation = 0.004 Å). The N4/O1/O2 nitro group is almost coplanar with its attached aromatic ring [dihedral angle = 3.9(2)°] and this conformation is supported by an intramolecular N3–H1n···O2 hydrogen bond [H···O = 1.97(3) Å, N–H···O = 134(3)°], which closes an *S*(6) ring. The *N*-butyl N3/C14–C17 side chain has an extended conformation as shown by the following torsion angles: C10–N3–C14–C15 = 174.5(2)°; N3–C14–C15–C16 = −174.2(2)°; C14–C15–C16–C17 = −178.9(2)°. The C3–O1, C1–C2, C2–C3, C4–C5 and C6–N1 bond lengths are 1.250(3), 1.364(4), 1.443(4), 1.329(4) and 1.301(3) Å, respectively. The C=O bond is slightly lengthed compared to a typical 'isolated' C=O double bond of ≈1.20 Å and C1–C2 is longer than C4–C5, suggesting a degree of intramolecular charge transfer from the amine N2 atom, which may affect the optical properties of this material. In the extended structure, two weak C–H···O interactions link the molecules into inversion dimers and numerous short π-π stacking contacts may help to consolidate the packing. The IR stretch of the C=O bond was also low at 1601 cm^{-1} indicative of a longer C=O bond. The HOMO-LUMO gap of 223 $kJ\,mol^{-1}$ was calculated from the UV/Vis spectrum, λ_{max} 534 nm (sh), or $\Delta E = Nhc/\lambda$ where N=Avogadro's number, h = Planck's constant and c = velocity of light.

The Hirshfeld surface[43–44] for compound **6** (Figure 2) shows red spots corresponding to the C–H···O hydrogen bonds associated with C2 and C13 as donors and O1 as the acceptor of both interactions. The major percentage contributors to the surface are H···H (41.6%), H···O/O···H (28.7%), C···H/H···C (9.1%) and C···C (8.5%).

At first we thought that the starting material **3** had undergone displacement of the alternative nitro group followed by oxidation to product **6**. However, if this was the case it was not clear why only old batches of the starting material were giving this additional product. We then decided to check carefully the composition of old batches of the starting material (Scheme 3). Samples were purified by chromatography on flash silica with gradient elution. Some starting material was eluted followed by compound **7** then compound **8**,[39] which was characterised by diffraction measurements (Figure 3). Compound **7** was fully characterised and its structure was inferred from the structure of the butylamine displacement product **6**. Two pathways are apparent for the oxidation or rearrangement of 5-methyl-2,3-dinitro-5,10-dihydrophenazine **3** The minor pathway leads to compound **7** and the major pathway 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.

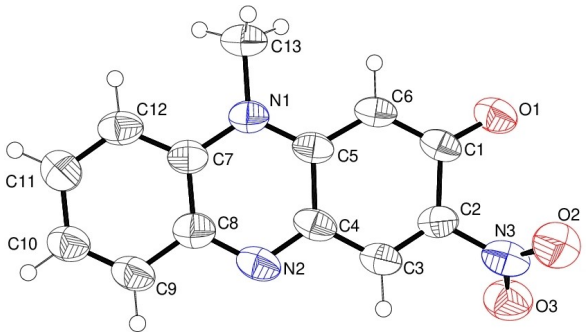


Figure 3. The molecular structure of compound **8** showing 50% displacement ellipsoids.

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

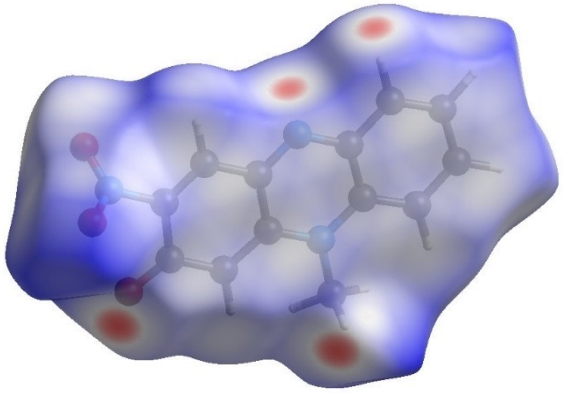
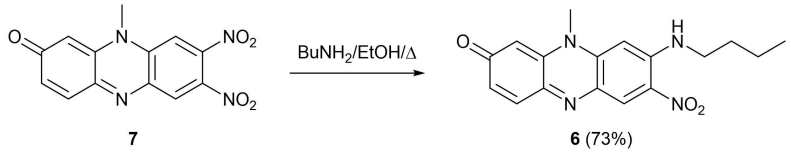
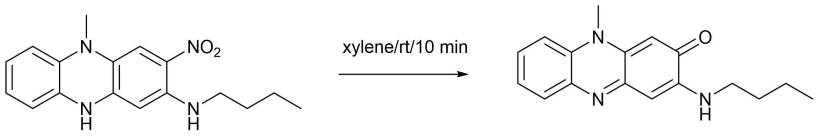


Figure 4. The Hirshfeld surface for compound **8** plotted over d_{norm} (−0.29 to 1.41 a.u.) showing red spots in the vicinities of atoms C6, C12, C13, O1, O3 and N1, corresponding to directional intermolecular contacts.



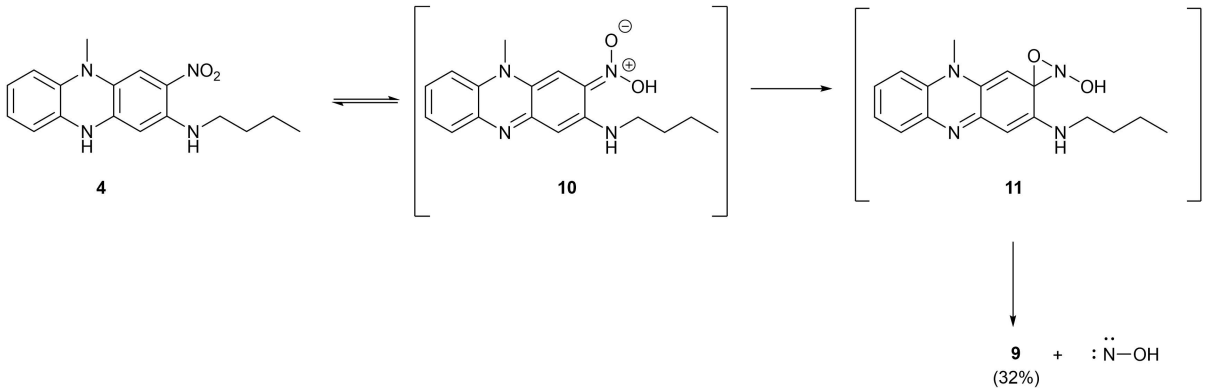
7 **6** (73%)

Scheme 4. The nucleophilic displacement of an activated nitro group by butylamine.



4 **9** (32%)

Scheme 5. The spontaneous rearrangement of compound **4** to phenazinone **9** in xylene.



4 **10** **11**

9 (32%) + :N—OH

Scheme 6. Proposed pathway for the spontaneous fragmentation of compound **4** in xylene at room temperature.

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 N1 conjugation. For compound **8** (λ_{max} = 534 nm), the HOMO-LUMO gap or $\Delta E = Nhc/\lambda = 223\ kJ\,mol^{-1}$ 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(10*H*)-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 R_f values. A TLC plate eluted with Et_2O/MeOH (99.5:0.5) distinguished the brighter red compound from the less polar red starting material (R_f = 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.[45] One possibility might involve a type of *cis-aci-nitro* form[46] **10** fragmenting (Scheme 6).

Conclusion

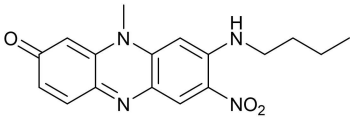
A new product has been isolated from the reaction of butylamine with 5-methyl-2,3-dinitro-5,10-dihydrophenazine **3** that had been stored in the dark for eight weeks in a sealed sample vial. The structure of this product, 8-(butylamino)-10-methyl-7-nitrophenazin-2(10*H*)-one **6**, was proven by an 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(10*H*)-one **7** and 10-methyl-3-nitrophenazin-2-(10*H*)-one **8**.[37] 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(10*H*)-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 have a low HOMO-LUMO energy gap. These studies are helpful for the goal of making 1,4-dihydroheteroacenes by illustrating the high reactivity of the phenazine secondary amine, even when it is conjugated to a nitro group, and it either needs to be substituted or sterically hindered. Disubstituted 1,4-dihydrophenazines are more puckered,[36] so are likely to be harder to make.

Experimental Section

IR spectra were recorded on a diamond Attuenated 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, δ, 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.

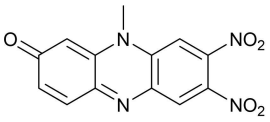
8-(Butylamino)-10-methyl-7-nitrophenazin-2(10*H*)-one 6



A batch of 5-methyl-2,3-dinitro-5,10-dihydrophenazine **3** that was over 8 weeks old and stored in a sealed vial (50 mg, 0.175 mmol) was dissolved in EtOH (50 mL) was treated with butylamine (64 mg, 0.874 mmol, 5 eq) and Hünig's base (113 mg, 0.874 mmol, 5 equiv.) and heated under reflux for 24 h. After cooling the mixture was diluted with water (200 mL) and mixed with aq. conc. HCl (5 mL) and extracted with CH_2Cl_2 (100 mL). The CH_2Cl_2 layer was then washed with water (200 mL), dried over $MgSO_4$, filtered and evaporated to dryness. The products were purified by chromatography on silica gel. CH_2Cl_2 eluted the starting material (7 mg, 14%), Et_2O, then MeOH/Et_2O (1:99) eluted 2-(butylamino)-5-methyl-3-nitro-5,10-dihydrophenazine **4**[39] (8 mg, 15%) and MeOH/Et_2O (10:90) eluted the title compound **6** (5 mg, 8%), mp: $>200\,^{\circ}C$ (from dichloromethane:light petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) 0.95-0.98 (3H, t, $J=8.0$), 1.45–1.52 (2H, m), 1.72–1.79 (2H, m), 3.29–3.34 (2H, q, $J=8.0$), 3.57 (3H, s), 6.10 (1H, s), 6.29 (1H, s), 6.82–6.84 (1H, d, $J=8.0$), 7.41–7.43 (2H, d, $J=8.0$), 8.30-8.35 (1H, s, br) and 8.70 (1H, s); ^{13}C NMR (100.1 MHz, D_7DMF, 25 °C) 13.4, 20.1, 30.4, 33.5, 42.9, 94.5, 102.1, 126.9, 129.7, 129.9, 133.4, 135.5, 138.3, 138.7, 145.6, 147.1 and 183.9 (C=O); λ_{max} (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(m) cm^{-1}; UV/Vis (EtOH): λ_{max} (ε) = 534sh (10,000), 509 nm (12,610), 413sh (2,520), 339 (7,900), 248 nm (10,000 $mol^{-1}\,dm^3\,cm^{-1}$); HRMS (ASAP Orbitrap) *m/z* calcd for $C_{17}H_{18}N_4O_3+H^+$: 327.1452; found: 327.1452 (100%).

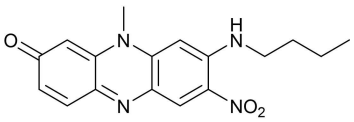
10-Methyl-7,8-dinitrophenazin-2(10*H*)-one 7



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. CH_2Cl_2 eluted the starting material (10 mg, 67%), then CH_2Cl_2/MeOH (10:90) eluted the title compound **7** (1 mg, 6%), then 10-methyl-3-nitrophenazin-2-(10*H*)-one[39] **8** (4 mg, 30%), mp: $>200\,^{\circ}C$ (from dichloromethane:light petroleum ether).

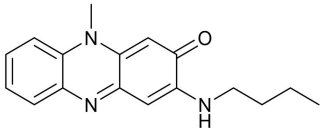
^{1}H NMR (400 MHz, D_7DMF, 25 °C) 4.14 (3H, s), 6.52 (1H, s), 7.24 (1H, d, $J=8.0$), 7.89 (1H, d, $J=8.0$), 8.21 (1H, s) and 8.84 (1H, s); ^{13}C NMR (100.1 MHz, D_7DMF, 25 °C) 102.9, 112.6, 128.5, 135.2, 135.2, 135.4, 137.0, 137.4, 138.1, 145.0, 152.7 and 184.2 (C=O); λ_{max} (ATR Diamond)(cm^{-1}) 3054(w), 1632(w), 1604(s), 1544(vs), 1467(s), 1331(vs), 1273(s), 1237(s), 1112(w), 1053(w), 927(w), 860(vs), 840(vs), 804(vs), 747(w), 594(w), 523(w), 475(s), 430(w) cm^{-1}; UV/Vis (EtOH): λ_{max} (ε) = 509 (1580), 314 nm (3160), 268 nm (3170 $mol^{-1}\,dm^3\,cm^{-1}$); HRMS (ASAP Orbitrap) *m/z* calcd for $C_{13}H_8N_4O_5+H^+$: 301.0567; found: 301.0570 (100%).

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



10-Methyl-7,8-dinitrophenazin-2(10*H*)-one **7** (5 mg, 0.0167 mmol) in EtOH (50 mL) was treated with $BuNH_2$ (20 mg, 0.274 mmol) and Hünig's base (20 mg, 0.155 mmol) and refluxed for 24 h. After cooling the mixture was diluted with water (200 mL) mixed with aq. conc. HCl (5 mL) and extracted with CH_2Cl_2 (100 mL). The CH_2Cl_2 layer was then washed with water (200 mL), dried over $MgSO_4$, filtered and evaporated to dryness. The products were purified by chromatography on silica gel. Elution with MeOH/Et_2O (10:90) gave the title compound **6** (4 mg, 73%) with identical spectroscopic properties to that reported previously in this paper.

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



2-(Butylamino)-5-methyl-3-nitro-5,10-dihydrophenazine **4** (10 mg, 0.0321 mmol) was dissolved in xylene (20 mL) and left at room temperature for 10 min. The solution turned from purple to yellow in minutes. A solution in EtOH is stable. The xylene mixture was then loaded onto a silica column and eluted with CH_2Cl_2 to remove

the xylene. Elution with MeOH/Et_2O (10:90) gave the title compound **9** (3 mg, 32%), mp: >200 °C (from dichloromethane: light petroleum ether).

^{1}H NMR (400 MHz, D_7DMF, 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), 6.79-6.88 (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); ^{13}C NMR (100.1 MHz, D_7DMF, 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 (C=O); λ_{max} (ATR Diamond)(cm^{-1}) 3252(w), 2956(w), 2926(w), 2857(w), 1661(w), 1621(w), 1539(vs), 1503(vs), 1470(s), 1373(w), 1329(w), 1231(w), 1164(w), 1033(w), 836(w), 747(vs), 579(s), 458(w) cm^{-1}; UV/Vis (EtOH): λ_{max} (ε)=445 (2510), 268 nm (3980 mol^{-1} dm^3 cm^{-1}); HRMS (ASAP Orbitrap) *m/z* calcd for $C_{17}H_{19}N_3O+H^+$: 282.1601; found: 282.1603 (100%).

Single-Crystal Diffraction

The crystal structures of compound **6** (red plate 0.06×0.04×0.01 mm) and compound **8** (purple blade 0.18×0.04×≈0.005 mm) were established using intensity data collected on a Rigaku AFC11 CCD diffractometer (Cu-K_α radiation, λ=1.54178 Å) at 100 K. The structures were routinely solved by dual-space methods using SHELXT[47] and the structural models were completed and optimized by refinement against $|F|^2$ with SHELXL-2018.[48] The N-bound H atom in compound **6** was located in a difference map and its position freely refined. The C-bound H atoms in both structures were placed geometrically (C–H=0.95–0.99 Å) and refined as riding atoms. The constraint U_{iso}(H)=1.2U_{eq}(carrier) or 1.5U_{eq}(methyl carrier) was applied in all cases. Full details of the structures and refinements are available in the deposited cifs. The data quality for compound **8** is poor, which is presumably reflected in the high residuals, but the structure has been unambiguously established.

Crystal data for compound **6** ($C_{17}H_{18}N_4O_3$): M_r=326.35, monoclinic, space group $P2_1/c$ (No. 14), a=12.6523(6) Å, b=16.4905(14) Å, c=7.3541(5) Å, β=99.158(5)°, V=1514.82(18) Å^3, Z=4, T=100 K, μ=0.830 mm^{-1}, ρ_{calc}=1.431 g cm^{-3}, 13791 reflections measured (7.1≤2θ≤149.9°), 2975 unique (R_{int}=0.052), $R(F)$=0.064 [2221 reflections with $I>2\sigma(I)$], $wR(F^2)$=0.186 (all data), $\Delta\rho_{min,max}$ (e Å^{-3})=−0.24, +0.50.

Crystal data for compound **8** ($C_{13}H_9N_3O_3$): M_r=255.23, monoclinic, space group $P2_1/c$ (No. 14), a=13.564(2) Å, b=3.8153(6) Å, c=21.370(4) Å, β=90.341(17)°, V=1105.8(3) Å^3, Z=4, T=100 K, μ=0.942 mm^{-1}, ρ_{calc}=1.533 g cm^{-3}, 12646 reflections measured (6.5≤2θ≤133.2°), 1961 unique (R_{int}=0.164), $R(F)$=0.145 [924 reflections with $I>2\sigma(I)$], $wR(F^2)$=0.435 (all data), $\Delta\rho_{min,max}$ (e Å^{-3})=−0.44, +0.79.

Supplemental Material

Deposition Numbers 2166565 (for **6**) and 216650 (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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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.

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