

# A paddle-wheel motif *versus* an extended network: two crystalline forms of 2,4-bis(phenylamino)nitrobenzene

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2,4-Difluoronitrobenzene is reacted with either one or two amines selected from aniline, ammonia, butylamine and benzylamine. All products are characterised spectroscopically and by single-crystal structure determinations. When formed as a minor component alongside 4-dimethylamino-2-(phenylamino)nitrobenzene, 2,4-bis(phenylamino)nitrobenzene crystallises as a hydrogen-bonded hexamer, or paddle-wheel motif, encompassing one-dimensional channels, but as a dense framework when pure. 2,4-Bis(butylamino)nitrobenzene crystallises with the same hexamer motif but with offset sheets.

**Keywords:** paddle-wheel motif, hexamer motif, channel, hydrogen bond, 2,4-bis(phenylamino)nitrobenzene

Clathrate-forming compounds such as cyclodextrins can crystallise with guests such as methyl orange, ferrocene and sodium 12-crown-4 to give a channel type arrangement of guests in the lattice.<sup>1–4</sup> These materials are of interest in separation science. For example, urea can be used to separate *n*-alkanes from kerosene.<sup>5–7</sup> Cyclic peptides can arrange into nanotubes, observed with electron microscopy, by hydrogen-bond directed self-assembly and serve as micropores in membranes.<sup>8,9</sup> These examples illustrate the vital role that crystal packing forces and molecular structure play in the design of novel solids that may have uses and functional applications. We now report our serendipitous discovery of a new class of compounds, which may either crystallise as hydrogen-bonded cyclic motifs or as dense, infinite networks.

## Discussion

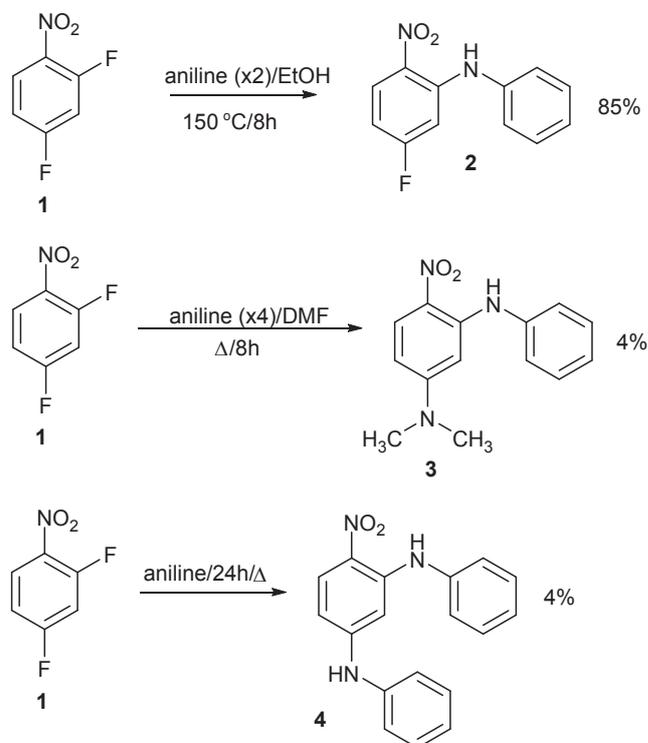
Our ongoing programme on the synthesis of mauveine derivatives<sup>10–14</sup> required some specialised aromatic building blocks, which we attempted to prepare by reacting 2,4-difluoronitrobenzene **1**, with aniline (Scheme 1). The nitro group activates both fluorine substituents to nucleophilic displacement. The first fluorine atom reacts easily to give 4-fluoro-2-(phenylamino)nitrobenzene **2**, in good yield.

Spectroscopic characterisation of product **2** did not confirm whether an *ortho* or *para* isomer had formed, but an X-ray crystal structure showed that the product is the *ortho* isomer **2** (Fig. 1). Even if **1** is heated with an excess of aniline in ethanol, the second fluorine atom in the *para* position is very slow to be substituted. The reaction of compound **1** with aniline in refluxing dimethylformamide (DMF) was attempted, as it is a higher boiling solvent, but this time 4-dimethylamino-2-(phenylamino)nitrobenzene **3** was formed in low yield, as confirmed by the X-ray single crystal structure (Fig. 1). The dimethylamine is probably liberated from DMF by a transamidation<sup>15–18</sup> reaction with aniline because the thermal decomposition of DMF, liberating dimethylamine and CO, is too slow.<sup>19</sup> Also, compound **2** did not give compound **3** when refluxed in DMF for 8 h. We conclude that initially, the aniline reacts at the *ortho* position, followed by the reaction of dimethylamine at the less reactive *para* position.

Finally, compound **1** was refluxed in pure aniline for 24 h or longer, which gave a low yield of the di-substituted product **4**. The remainder of the material was the mono(phenylamino)-substituted product **2**, which was discarded. The spectroscopic data for **4** are as expected apart from one NH signal, which is absent for this derivative. Since compounds **2** and **3** show

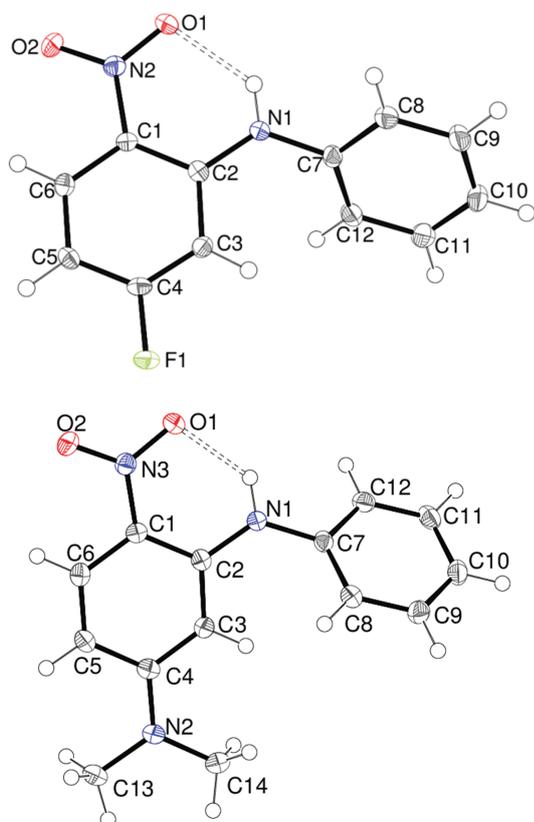
just one NH signal beyond 9 ppm, it must be the NH signal for the *para* amino group that is missing. Presumably the fast inter-conversion of two conformational isomers broadens this NH signal. Interestingly two possible conformational isomers are seen by comparing the two crystal structures of 2,4-bis(phenylamino)nitrobenzene **4**, **4a** and **4b**. Two completely different crystal structures were obtained (Fig. 2). The first structure **4a**, which probably incorporates solvent molecules, was a minor side product, a yellow needle, in a batch of compound **3**, which formed as orange plates. Compound **3** appeared to be pure as characterised by NMR spectroscopy, so the amount of **4a** must be very small and there was not enough to carry out elemental analysis. A second, identical X-ray data set was also collected for compound **4a**, when it crystallised as a minor side product with compound **5**, which is described later.

In the crystal of the first phase **4a**, m.p. 146–147 °C, the molecules of **4** are linked by side-by-side N–H and C–H hydrogen bonds to generate a cyclic hexamer motif; these units stack on top of each other to form large [001] channels (Fig. 3)



**Scheme 1** The reactions of 2,4-difluoronitrobenzene **1** with aniline in ethanol or DMF or neat to form compounds **2**, **3** and **4** respectively.

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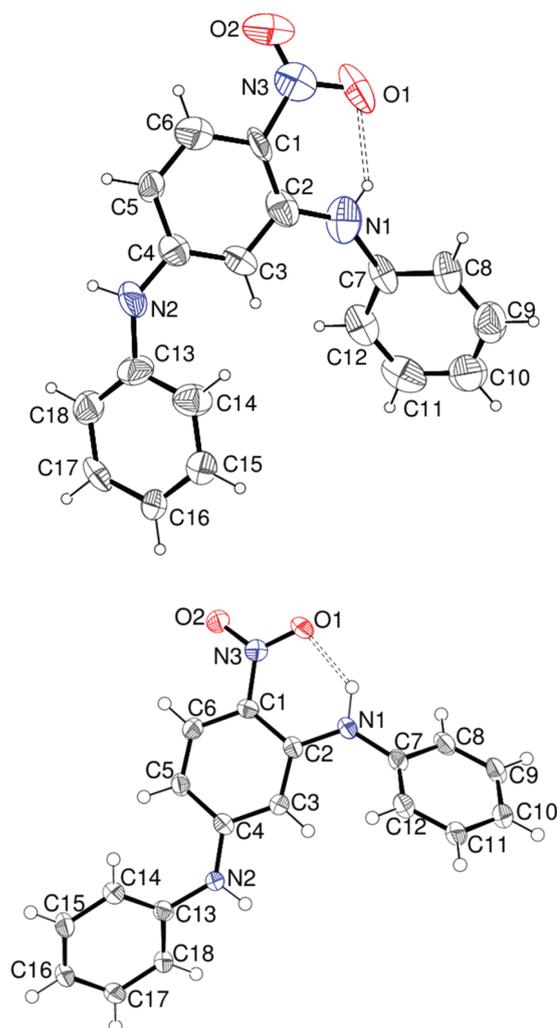


**Fig. 1** The molecular structures of **2** (top) and **3** (bottom) showing 50% displacement ellipsoids, with the intramolecular N–HO hydrogen bond indicated by a double-dashed line. The dihedral angle between the aromatic rings is 49.28 (4)° in **2** and 44.85 (4)° in **3**.

of approximate diameter 10.5 Å, assuming a Van der Waals' radius of 1.4 Å for an O atom. The channels are presumably filled with disordered solvent molecules, although these could not be discerned in the present experiment. The second phase **4b** was obtained from the crystallisation of compound **4** in a pure state, prepared by refluxing compound **1** in neat aniline, as described above, to yield fawn crystals, m.p. 169–170 °C, which is notably higher than that of **4a**. The crystal of **4b** is dense (*i.e.* there is a lack of solvent space or identifiable pores or channels) and the molecules are linked by N–HO hydrogen bonds to form infinite [010] chains. The open-framework compound **4a** could not be obtained by crystallising a pure sample of compound **4**, but only when compound **4** was formed as an impurity in samples **3** and **5**.

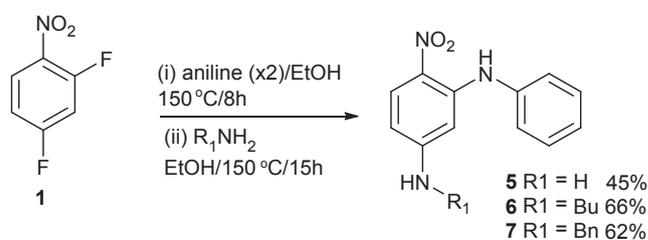
The crystallisation of the paddle-wheel motif is not straightforward and appears to depend upon the environment, although it can be reproduced. Open-framework structures usually only form in purely organic materials when clathrates occur, so this structure is novel and the two possible lattices, **4a** and **4b**, may be close in energy. Owing to the difficulty of preparing compound **4**, and the difficulty of crystallising lattice **4a** by this route, we prepared further derivatives **5–8** and determined their crystal structures in search of other possible paddle-wheel motifs.

The syntheses are all similar. After the reaction of 2,4-difluoronitrobenzene **1**, with aniline, a preliminary purification was performed by removing the ethanol solvent, but the intermediate compound **2** was not isolated and purified (Scheme 2). This explains why small traces of some 2,4-bis(phenylamino)nitrobenzene **4** were sometimes found in the products, such as compounds **3** and **5**. For example, when compound **5** was crystallised from ether/light petroleum ether

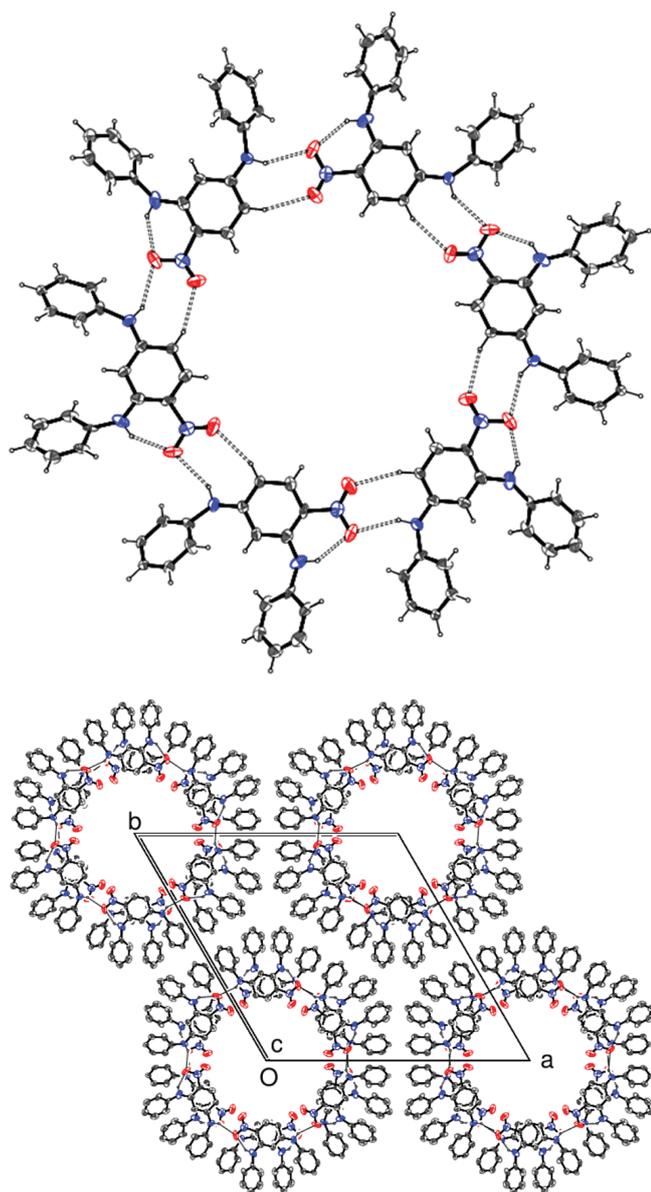


**Fig. 2** The molecular structures of **4a** (top) and **4b** (bottom) showing 25% and 50% displacement ellipsoids, respectively, with hydrogen bonds indicated by double-dashed lines. The dihedral angles between the central ring and the *ortho*- and *para*-bonded rings are 41.7 (5) and 41.1 (5)°, respectively in **4a** and 42.83 (8) and 41.43 (10)°, respectively, in **4b**. These values are very similar, but the overall molecular conformations are quite different, as indicated by the C3–C4–N2–C13 torsion angles of 6 (2) and 174.3 (3)° for **4a** and **4b**, respectively and the H2–N2–C4–C5 torsion angles of 5 and 162° for **4a** and **4b**, respectively.

40–60, it gave orange blocks of 4-amino-2-(phenylamino)nitrobenzene **5** along with a small quantity of yellow needles of 2,4-bis(phenylamino)nitrobenzene **4a**. This time the yellow needles were easy to see as a side product in the material. The crystal structure derived from one of them was the same hexamer motif **4a** or channel framework as described above. However, the hydrogen-bonding arrangements in compounds **5** and **6** (Figs 4 and 5) lead to extended dense networks and not to an open framework with channels.

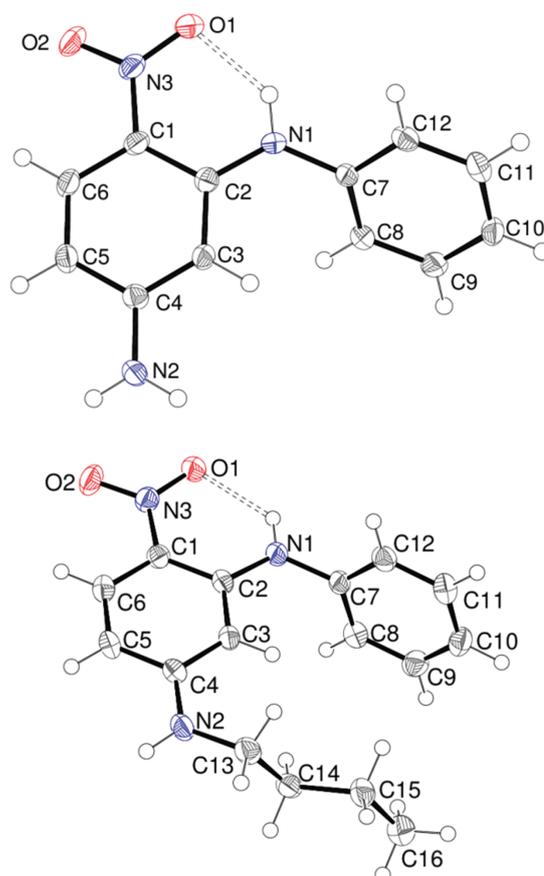


**Scheme 2** Reaction of 2,4-difluoronitrobenzene **1** with aniline followed by  $\text{NH}_4\text{OH}$ ,  $\text{BuNH}_2$  and  $\text{BnNH}_2$  to prepare compounds **5**, **6** and **7** respectively.



**Fig. 3** A hexameric hydrogen-bonded ring with graph-set motif  $R_6^6(48)$  for the N–H hydrogen bonds in the crystal of **4a** (top) and the unit-cell packing in **4a** viewed down [001] (bottom), showing the formation of one-dimensional channels. A PLATON<sup>20</sup> analysis of the structure indicated the volume of free space to be 753 Å<sup>3</sup> per unit cell (14.4% of the cell volume).

Through persisting at the bench, we also prepared 2,4-bis(butylamino)nitrobenzene **8**, by reacting an excess of BuNH<sub>2</sub> with 2,4-difluoronitrobenzene **1** (Scheme 3). This was a very clean reaction in a yield of 84%. Luckily, the sought after cyclic hexamer motif with identical side-by-side N–H and C–H hydrogen bonds was observed in the crystal structure of this compound (Fig. 6). However, the rhombohedral crystal symmetry in **8**, rather than the hexagonal symmetry in **4a**, dictates that the hexamers are laterally displaced between layers and no channels are apparent. Three butyl groups block each channel. Nevertheless this structure demonstrates that the hexameric cyclic motif is not just restricted to 2,4-bis(phenylamino)nitrobenzene **4a**. An attempt to form clathrates of compound **8** from ether/light petroleum ether with biphenyl, 4,4-dipyridyl, azobenzene, 1,6-bis(4-pyridyl)hexane and a number of other flexible dipyridyls available to us, was unsuccessful. In each case the crystals harvested were those of starting material **8**, as shown by the determination of their unit cells.



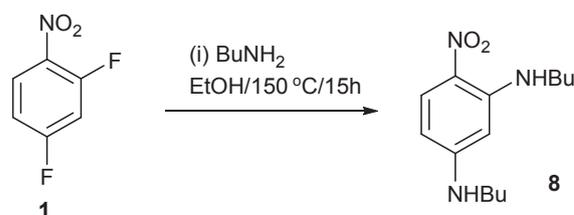
**Fig. 4** The molecular structures of the C1-containing molecule in **5** (top) and the C1-containing molecule in **6** (bottom) showing 50% displacement ellipsoids, with hydrogen bonds indicated by double-dashed lines. Compound **5** contains three molecules in the asymmetric unit, with dihedral angles between the aromatic rings of 49.17 (5), 67.37 (4) and 45.95 (5)°. Compound **6** contains four molecules in the asymmetric unit, with dihedral angles between the aromatic rings of 79.82 (6), 73.85 (7), 79.14 (5) and 64.40 (6)°.

## Experimental

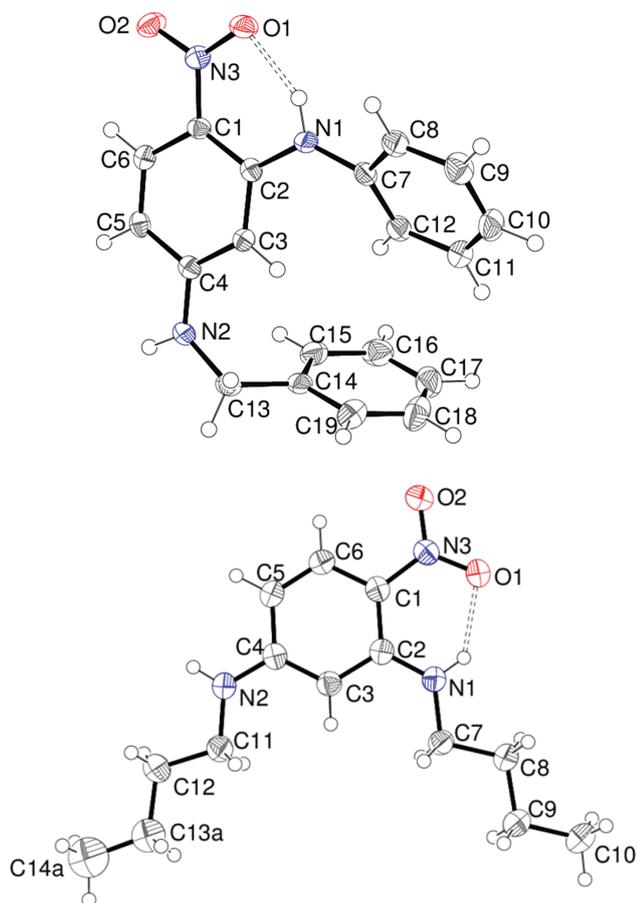
IR spectra were recorded on an ATI Mattson FTIR spectrometer using KBr discs. UV spectra were recorded using a Perkin-Elmer Lambda 25 UV-Vis spectrometer with CH<sub>2</sub>Cl<sub>2</sub> as the solvent. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 400 MHz and 100.5 MHz, respectively, 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. Low resolution and high resolution mass spectra were obtained at the University of Wales, Swansea using electron impact ionisation and chemical ionisation. Melting points were determined on a Kofler hot-stage microscope.

### Crystal growth

For all samples, the starting material was dissolved in ether (10–50 mL) and diluted with light petroleum ether 40–60 (10–50 mL), and left to evaporate slowly at room temperature.



**Scheme 3** Reaction of 2,4-difluoronitrobenzene **1** with BuNH<sub>2</sub>



**Fig. 5** The molecular structures of **7** (top) and **8** (bottom) showing 50% displacement ellipsoids, with hydrogen bonds indicated by double-dashed lines. The C11-butyl chain in **8** is disordered over two orientations in a 0.549 (12):0.451 (12) ratio. The dihedral angles between the central and C7- and C14-rings in **7** are 37.98 (6) and 76.12 (4)° respectively.

### Crystallography

The intensity data for **2–8** (except **4a**) were collected on a Rigaku Mercury CCD diffractometer (MoK $\alpha$  radiation,  $\lambda=0.71073$  Å,  $T=100$  K); those for **4a** were collected at beam-line I19 at the Diamond Synchrotron Source ( $\lambda=0.68890$  Å,  $T=298$  K). The structures were solved by direct methods with SHELXS-97<sup>21</sup> and the structural models completed and refined against  $|F|^2$  with SHELXL-97.<sup>21</sup> The N-bound H atoms were located in difference maps and either refined freely or as riding atoms in their as-found relative positions. The C-bound H atoms were placed in idealised locations and refined as riding atoms. The constraint  $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{carrier})$  or  $1.5U_{\text{eq}}(\text{methyl C})$  was applied in all cases.

The diffracting power, even for data collected on a synchrotron, was extremely poor for **4a**, although the structure was clearly discernible. The benzene rings were modelled as rigid hexagons with a side-length of 1.39 Å and similarity restraints on  $U_{ij}$  values were applied. The geometry of the nitro group was maintained with a planarity restraint. Difference Fourier maps in the region of the [001] channels were essentially featureless and could not be interpreted as disordered solvent molecules: the contribution to the scattering was removed with the SQUEEZE routine in PLATON.<sup>20</sup>

The CCDC reference numbers given below contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request.cif](http://www.ccdc.cam.ac.uk/data_request.cif).

**2:** C<sub>12</sub>H<sub>9</sub>FN<sub>2</sub>O<sub>2</sub>,  $M_r=232.21$ , orange rod,  $0.42 \times 0.05 \times 0.04$  mm, orthorhombic, space group *Pbca* (No. 61),  $Z=8$ ,  $a=12.6596$  (9),  $b=7.9294$  (5),  $c=20.8034$  (14) Å,  $V=2088.3$  (2) Å<sup>3</sup> at 100 K. Number of measured and unique reflections=13570 and 2398, respectively

( $-16 \leq h \leq 16$ ,  $-10 \leq k \leq 10$ ,  $-26 \leq l \leq 26$ ;  $2\theta_{\text{max}}=52.0^\circ$ ;  $R_{\text{int}}=0.048$ ). Final  $R(F)=0.036$ ,  $wR(F^2)=0.093$  for 157 parameters and 1879 reflections with  $I > 2\sigma(I)$  (corresponding  $R$ -values based on all 2398 reflections=0.049 and 0.100, respectively), CCDC reference number 1026369.

**3:** C<sub>14</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>,  $M_r=257.29$ , orange plate,  $0.23 \times 0.11 \times 0.02$  mm, monoclinic, space group *P2<sub>1</sub>/c* (No. 14),  $Z=4$ ,  $a=11.6236$  (8),  $b=6.6269$  (5),  $c=17.1321$  (11) Å,  $\beta=107.1480$  (14)°,  $V=1260.99$  (15) Å<sup>3</sup> at 100 K. Number of measured and unique reflections=13572 and 2893, respectively ( $-14 \leq h \leq 15$ ,  $-8 \leq k \leq 8$ ,  $-22 \leq l \leq 22$ ;  $2\theta_{\text{max}}=55.0^\circ$ ;  $R_{\text{int}}=0.041$ ). Final  $R(F)=0.041$ ,  $wR(F^2)=0.121$  for 177 parameters and 2400 reflections with  $I > 2\sigma(I)$  (corresponding  $R$ -values based on all 2893 reflections=0.048 and 0.127, respectively), CCDC reference number 1026370.

**4a:** C<sub>18</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>,  $M_r=305.33$ , yellow needle,  $0.08 \times 0.01 \times 0.01$  mm, hexagonal, space group *P6cc* (No. 184),  $Z=12$ ,  $a=28.807$  (16),  $c=7.300$  (4) Å,  $V=5246$  (5) Å<sup>3</sup> at 298 K. Number of measured and unique reflections=20009 and 994, respectively ( $-28 \leq h \leq 27$ ,  $-27 \leq k \leq 28$ ,  $-7 \leq l \leq 6$ ;  $2\theta_{\text{max}}=40.0^\circ$ ;  $R_{\text{int}}=0.075$ ). Final  $R(F)=0.189$ ,  $wR(F^2)=0.494$  for 169 parameters and 984 reflections with  $I > 2\sigma(I)$  (corresponding  $R$ -values based on all 994 reflections=0.190 and 0.496, respectively), CCDC reference number 1026371. The unidentified solvent is not included in the calculations of  $M_r$ , etc.

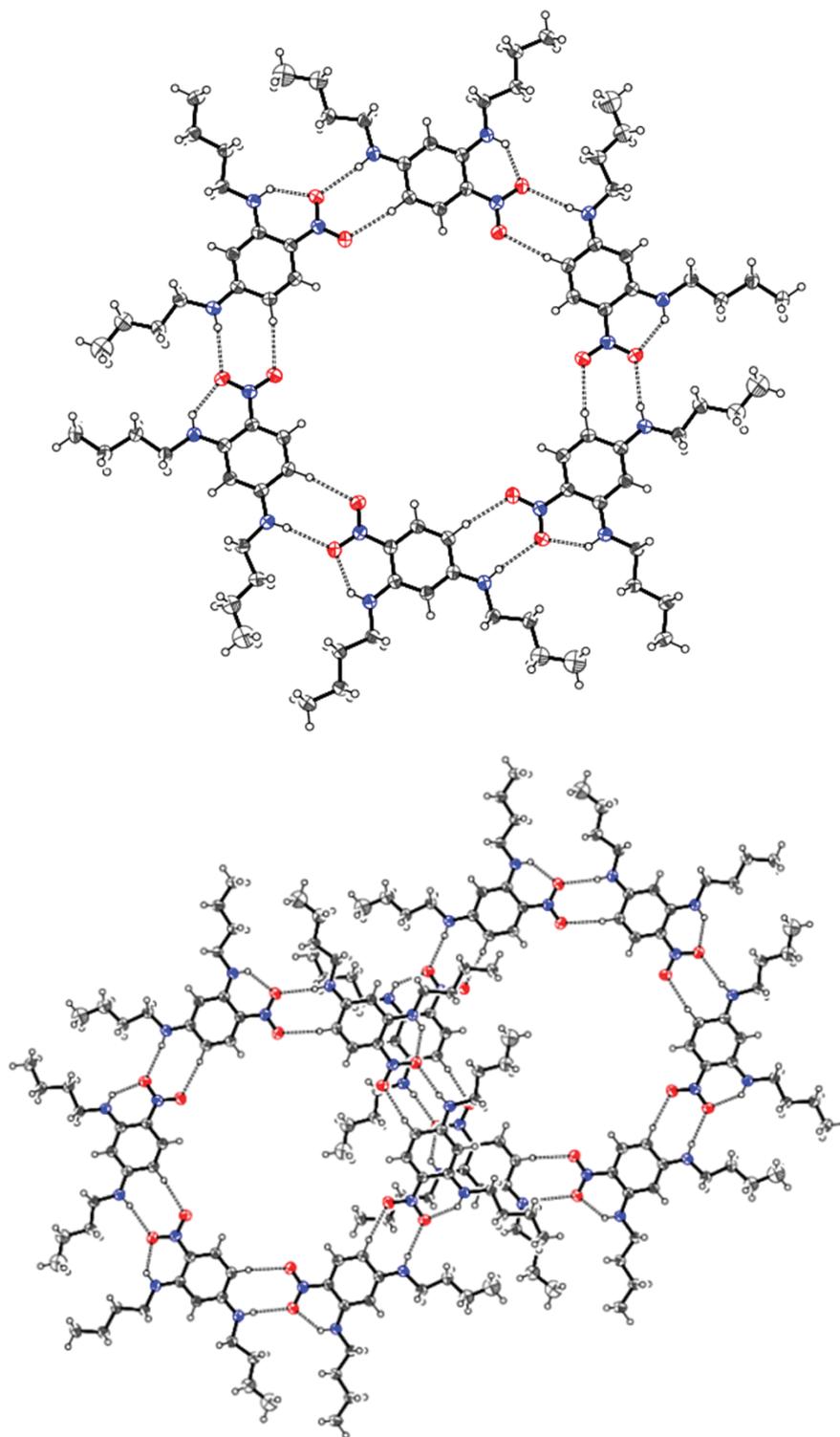
**4b:** C<sub>18</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>,  $M_r=305.33$ , yellow lath-like,  $0.22 \times 0.05 \times 0.01$  mm, monoclinic, space group *P2<sub>1</sub>/c* (No. 14),  $Z=4$ ,  $a=13.347$  (6),  $b=15.571$  (7),  $c=7.222$  (4) Å,  $\beta=104.416$  (9)°,  $V=1453.7$  (12) Å<sup>3</sup> at 100 K. Number of measured and unique reflections=15902 and 2579, respectively ( $-15 \leq h \leq 15$ ,  $-18 \leq k \leq 18$ ,  $-8 \leq l \leq 8$ ;  $2\theta_{\text{max}}=50.2^\circ$ ;  $R_{\text{int}}=0.148$ ). Final  $R(F)=0.049$ ,  $wR(F^2)=0.102$  for 214 parameters and 1447 reflections with  $I > 2\sigma(I)$  (corresponding  $R$ -values based on all 2579 reflections=0.107 and 0.123, respectively), CCDC reference number 1026372.

**5:** C<sub>12</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub>,  $M_r=229.24$ , red block,  $0.50 \times 0.45 \times 0.19$  mm, monoclinic, space group *P2<sub>1</sub>/c* (No. 14),  $Z=12$ ,  $a=13.5737$  (10),  $b=15.6234$  (11),  $c=16.7015$  (11) Å,  $\beta=113.4950$  (16)°,  $V=3248.2$  (4) Å<sup>3</sup> at 100 K. Number of measured and unique reflections=21009 and 7408, respectively ( $-17 \leq h \leq 17$ ,  $-20 \leq k \leq 20$ ,  $-21 \leq l \leq 18$ ;  $2\theta_{\text{max}}=55.0^\circ$ ;  $R_{\text{int}}=0.037$ ). Final  $R(F)=0.038$ ,  $wR(F^2)=0.088$  for 488 parameters and 5278 reflections with  $I > 2\sigma(I)$  (corresponding  $R$ -values based on all 7408 reflections=0.063 and 0.095, respectively), CCDC reference number 1026373.

**6:** C<sub>16</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub>,  $M_r=285.34$ , yellow block,  $0.20 \times 0.18 \times 0.04$  mm, triclinic, space group *P $\bar{1}$*  (No. 2),  $Z=8$ ,  $a=10.9686$  (8),  $b=13.6711$  (10),  $c=19.8392$  (14) Å,  $\alpha=85.091$  (4),  $\beta=84.013$  (4),  $\gamma=85.625$  (4)°,  $V=2941.0$  (4) Å<sup>3</sup> at 100 K. Number of measured and unique reflections=34235 and 10626, respectively ( $-13 \leq h \leq 12$ ,  $-16 \leq k \leq 16$ ,  $-23 \leq l \leq 23$ ;  $2\theta_{\text{max}}=50.5^\circ$ ;  $R_{\text{int}}=0.047$ ). Final  $R(F)=0.056$ ,  $wR(F^2)=0.143$  for 746 parameters and 8423 reflections with  $I > 2\sigma(I)$  (corresponding  $R$ -values based on all 10626 reflections=0.070 and 0.152, respectively), CCDC reference number 1026374.

**7:** C<sub>19</sub>H<sub>17</sub>N<sub>3</sub>O<sub>2</sub>,  $M_r=319.36$ , orange block,  $0.59 \times 0.17 \times 0.10$  mm, monoclinic, space group *P2<sub>1</sub>/c* (No. 14),  $Z=4$ ,  $a=7.5803$  (5),  $b=30.566$  (2),  $c=6.8976$  (5) Å,  $\beta=93.528$  (3)°,  $V=1595.14$  (19) Å<sup>3</sup> at 100 K. Number of measured and unique reflections=10712 and 3632, respectively ( $-9 \leq h \leq 9$ ,  $-39 \leq k \leq 39$ ,  $-8 \leq l \leq 8$ ;  $2\theta_{\text{max}}=55.0^\circ$ ;  $R_{\text{int}}=0.044$ ). Final  $R(F)=0.043$ ,  $wR(F^2)=0.088$  for 223 parameters and 2610 reflections with  $I > 2\sigma(I)$  (corresponding  $R$ -values based on all 3632 reflections=0.070 and 0.095, respectively), CCDC reference number 1026375.

**8:** C<sub>14</sub>H<sub>23</sub>N<sub>3</sub>O<sub>2</sub>,  $M_r=265.35$ , yellow block,  $0.11 \times 0.10 \times 0.04$  mm, trigonal, space group *R $\bar{3}$*  (No. 148),  $Z=18$ ,  $a=28.3820$  (19),  $c=10.3665$  (7) Å,  $V=7231.8$  (8) Å<sup>3</sup> at 100 K. Number of measured and unique reflections=29374 and 3679, respectively ( $-36 \leq h \leq 36$ ,  $-33 \leq k \leq 36$ ,  $-18 \leq l \leq 18$ ;  $2\theta_{\text{max}}=55.0^\circ$ ;  $R_{\text{int}}=0.067$ ). Final  $R(F)=0.077$ ,  $wR(F^2)=0.235$  for 180 parameters and 3098 reflections with  $I > 2\sigma(I)$  (corresponding  $R$ -values based on all 3679 reflections=0.087 and 0.247, respectively), CCDC reference number 1026376.



**Fig. 6** A hexameric hydrogen-bonded ring with graph-set motif  $R_6^6(48)$  for the N–HO hydrogen bonds in the crystal of **8** (top) and a pair of staggered hexamers viewed down [001] (bottom), showing how the protruding butyl groups lead to the formation of a network without channels. It is interesting, however, that PLATON indicates that there is still some 439 Å<sup>3</sup> of solvent-accessible space per unit cell (6.1% of the cell volume).

*4-Fluoro-2-(phenylamino)nitrobenzene (2)*: 2,4-Difluoronitrobenzene (500 mg, 3.10 mmol) in EtOH (5 mL) and aniline (585 mg, 6.20 mmol) were heated in a Teflon-lined Parr digestion bomb at 150 °C for 8 h. After cooling, crystals were present in the bomb. The ethanol was removed by pipette and the material was air dried. The product was purified by chromatography on silica gel. Elution with ether:light petroleum 40–60 (25:75) gave the title compound (611 mg, 85%) m.p. 93–94 °C (from ether/light petroleum ether 40–60).  $\lambda_{\text{max}}$  (EtOH)/nm 405 (log  $\epsilon$  3.68) and 260 (3.95);  $\lambda_{\text{max}}$  (KBr disc) 3325w, 1622m, 1579m, 1494m, 1414w, 1341w, 1323w, 1203s, 1076s, 993m, 852s, 811s, 748s,

733vs, 683s, 615s;  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 6.34 (1H, *t*,  $J=6.4$  and 5.6), 6.68 (1H, *d*,  $J=7.6$ ), 7.15–7.18 (3H, *m*), 7.33 (2H, *t*,  $J=4.8$  and 4.8), 8.12 (1H, *t*,  $J=5.0$  and 4.0) and 9.52 (1H, *s*);  $\delta_{\text{C}}$  (100.1 MHz; CDCl<sub>3</sub>) 101.2, 101.4, 105.8, 105.9, 124.8, 126.4, 129.7, 129.8, 129.9, 137.9, 145.5, 145.6, 166.3 and 168.0;  $m/z$  (orbitrap ASAP) 233.0716 ( $M^+ + H$ , 100%) C<sub>12</sub>H<sub>10</sub>FN<sub>2</sub>O<sub>2</sub> requires 233.0721.

*4-Dimethylamino-2-(phenylamino)nitrobenzene (3)*: 2,4-Difluoronitrobenzene (5.00 g, 0.0314 mol) and aniline (11.7 g, 0.126 moles) were refluxed in DMF (50 mL) for 8 h. After cooling, the mixture was diluted with aqueous HCl (2 M) and extracted with DCM (50 mL).

The organic layer was separated, dried over  $\text{MgSO}_4$ , filtered and concentrated under reduced pressure. Part of the product was purified by chromatography on silica gel. Elution with ether:light petroleum ether 40–60 (25:75) gave the title compound (350 mg, 4%) as a yellow solid, m.p. 138–139 °C (from ether/light petroleum ether 40–60).  $\lambda_{\text{max}}$  (EtOH)/nm 414 (log  $\epsilon$  4.24) and 276 (4.17);  $\nu_{\text{max}}$  (KBr disc) 3275w, 1617m, 1562m, 1532m, 1486s, 1267s, 1179s, 1153s, 908m, 810m, 764s, 742s, 605s, 572s, 500s and 548m;  $\delta_{\text{H}}$ (400 MHz;  $\text{CDCl}_3$ ) 2.90 (6H, s), 6.15–6.19 (2H, m), 7.19 (1H, t,  $J=8.0$  and 7.8), 7.30 (2H, d,  $J=8.0$ ), 7.39 (2H, t,  $J=6.8$  and 6.8), 8.10 (1H, d,  $J=9.6$ ) and 9.92 (1H, s);  $\delta_{\text{C}}$ (100.1 MHz;  $\text{CDCl}_3$ ) 40.1, 93.2, 104.4, 124.3, 125.2, 128.9, 129.6, 139.2, 145.4 and 155.0 (one peak is missing),  $m/z$  (orbitrap ASAP) 258.1237 ( $\text{M}^+\text{H}$ , 100%)  $\text{C}_{14}\text{H}_{16}\text{N}_3\text{O}_2$  requires 258.1237. When crystals were being selected for X-ray data collection, the title compound (as orange plates) and a trace amount of 2,4-bis(phenylamino)nitrobenzene **4a**, as yellow needles (m.p. 146–147 °C), were apparent.

**2,4-Bis(Phenylamino)nitrobenzene (4b):** 2,4-Difluoronitrobenzene (1.0 g, 6.29 mmol) in aniline (20 mL) was refluxed for 24 h. After cooling, ether (100 mL) was added and the mixture was extracted with aqueous HCl (20 mL  $\text{CHCl}_3$ :40 mL  $\text{H}_2\text{O}$ ) to remove excess aniline. The ether layer was dried over  $\text{MgSO}_4$  and concentrated under reduced pressure. The product was purified by chromatography on silica gel. Ether:light petroleum ether 40–60 (25:75) eluted the main yellow band contaminated with a red band. The product mixture was concentrated under reduced pressure to a dark solid and extracted with ether (30 mL  $\times$  3). This extract was concentrated to a solid under reduced pressure and then extracted with petroleum ether 40–60 (30 mL  $\times$  3). This extract was concentrated under reduced pressure to give the title compound (80 mg, 4%) as a fawn (glistening brown/yellow solid, m.p. 169–170 °C (from ether/light petroleum ether 40–60). Only a small amount of the product was purified.  $\lambda_{\text{max}}$  (EtOH)/nm 410 (log  $\epsilon$  3.97) and 265 (3.77);  $\nu_{\text{max}}$  (KBr disc) 3315w, 3046w, 1621w, 1585s, 1574s, 1537s, 1495s, 1470s, 1408w, 1303w, 1282s, 1205s, 1151s, 816w, 750s, 686s, 583s and 501s;  $\delta_{\text{H}}$ (400 MHz;  $\text{CDCl}_3$ ) 6.26 (1H, d,  $J=6.0$ ), 6.49 (1H, d,  $J=1.2$ ), 7.01–7.04 (3H, m), 7.11 (1H, t,  $J=8.4$  and 8.0), 7.18–7.19 (2H, m), 7.22 (2H, t,  $J=5.0$  and 5.2), 7.30 (2H, t,  $J=6.0$  and 5.2), 8.05 (1H, d,  $J=8.0$ ) and 9.77 (1H, s);  $\delta_{\text{C}}$ (100.1 MHz;  $\text{CDCl}_3$ ) 96.6, 106.6, 121.8, 124.4, 124.6, 125.5, 129.3, 129.5, 129.5, 138.7, 139.3, 145.7 and 150.8; (one peak is missing)  $m/z$  (orbitrap ASAP) 306.1236 ( $\text{M}^+\text{H}$ , 100%)  $\text{C}_{18}\text{H}_{16}\text{N}_3\text{O}_2$  requires 306.1237.

**4-Amino-2-(phenylamino)nitrobenzene (5):** 2,4-Difluoronitrobenzene (0.500 g, 3.14 mmol) and aniline (585 mg, 6.2 mmol) in EtOH (8 mL) were heated in a Teflon-lined Parr digestion bomb at 150 °C for 8 h. After cooling, the ethanol was removed by pipette then EtOH (4 mL) and  $\text{cNH}_3/\text{H}_2\text{O}$  (4 mL) was added. After sealing, the mixture was heated at 150 °C for 15 h. On cooling the mixture was mixed with DCM (50 mL) and extracted with  $\text{H}_2\text{O}$  (50 mL), then dried over  $\text{MgSO}_4$ , concentrated under reduced pressure and purified by chromatography on silica gel. Elution with ether:light petroleum ether 40–60 (25:75) gave the title compound (325 mg, 45%) as orange blocks, m.p. 123–124 °C (from ether/light petroleum ether 40–60).  $\lambda_{\text{max}}$  (EtOH)/nm 398 (log  $\epsilon$  4.05) and 277 (3.85);  $\nu_{\text{max}}$  (KBr disc) 3467w, 3433w, 3381w, 3346w, 3231w, 1612s, 1589s, 1561s, 1492vs, 1415s, 1273s, 1255s, 1214s, 1164s, 801s, 751vs, 690vs and 562s;  $\delta_{\text{H}}$ (400 MHz;  $\text{CDCl}_3$ ) 3.90–4.45 (2H, s), 6.04 (1H, dd,  $J=9.6$  and 2.4), 6.19 (1H, d,  $J=2.4$ ), 7.21 (1H, t,  $J=7.4$  and 7.6), 7.25 (2H, d,  $J=5.6$ ), 7.39 (2H, t,  $J=7.8$  and 7.2), 8.05 (1H, d,  $J=9.2$ ) and 9.83 (1H, s);  $\delta_{\text{C}}$ (100.1 MHz;  $\text{CDCl}_3$ ) 95.8, 106.8, 125.0, 125.3, 125.7, 129.5, 129.6, 138.7, 146.1 and 153.7;  $m/z$  (orbitrap ASAP) 230.0920 ( $\text{M}^+\text{H}$ , 100%)  $\text{C}_{12}\text{H}_{12}\text{N}_3\text{O}_2$  requires 230.0924. Fine yellow needles (3 mg, 0.3%) of compound **4a** were characterised by an X-ray single crystal structure determination, and had an identical unit cell to the material found as an impurity in compound **3**.

**4-Butylamino-2-(phenylamino)nitrobenzene (6):** 2,4-Difluoronitrobenzene (0.5 g, 3.14 mmol) and aniline (585 mg, 6.2 mmol) in EtOH (8 mL) were heated in a Teflon-lined Parr digestion bomb at 150 °C for 8 h. After cooling, the EtOH was removed by pipette. Then EtOH (4 mL) was added and an excess of butylamine (1.0 mL). After

sealing, the mixture was heated at 150 °C for 15 h. On cooling the mixture was mixed with DCM (50 mL), extracted with  $\text{H}_2\text{O}$  (50 mL), then dried over  $\text{MgSO}_4$ , concentrated under reduced pressure and purified by chromatography on silica gel. Elution with ether:light petroleum ether 40–60 (25:75) gave the title compound (590 mg, 66%) as a yellow solid, m.p. 75–76 °C (from ether/light petroleum ether 40–60).  $\lambda_{\text{max}}$  (EtOH)/nm 409 (log  $\epsilon$  4.42) and 276 (4.18);  $\nu_{\text{max}}$  (KBr disc) 3419w, 3329w, 1626m, 1613m, 1558m, 1411m, 1352m, 1262s, 1164s, 1105s, 962s, 804s, 756s, 548vs and 527vs;  $\delta_{\text{H}}$ (400 MHz;  $\text{CDCl}_3$ ) 0.90 (3H, t,  $J=7.2$ ), 1.34 (2H, s,  $J=7.2$ ), 1.55 (2H, p,  $J=7.6$ ), 3.04 (2H, t,  $J=6.8$ ), 6.03 (1H, d,  $J=10.0$ ), 6.12 (1H, s), 7.20 (1H, t,  $J=6.4$  and 6.8), 7.27 (2H, t,  $J=6.8$  and 6.0), 7.40 (2H, t,  $J=6.8$  and 6.4), 8.05 (1H, d,  $J=9.6$ ) and 9.97 (1H, s);  $\delta_{\text{C}}$ (100.1 MHz;  $\text{CDCl}_3$ ) 13.7, 20.1, 31.0, 43.0, 92.8, 106.1, 124.7, 125.4, 129.2, 129.6, 138.9, 146.2 and 154.1 (one peak is missing);  $m/z$  (orbitrap ASAP) 286.1552 ( $\text{M}^+\text{H}$ , 100%)  $\text{C}_{16}\text{H}_{20}\text{N}_3\text{O}_2$  requires 286.1550.

**4-Benzylamino-2-(phenylamino)nitrobenzene (7):** 2,4-Difluoronitrobenzene (0.5 g, 3.14 mmol) and aniline (585 mg, 6.2 mmol) in EtOH (8 mL) were heated in a Teflon-lined Parr digestion bomb at 150 °C for 8 h. After cooling, the EtOH was removed by pipette and then EtOH (4 mL) and benzylamine (672 mg, 6.28 mmol) were added. After sealing, the mixture was heated at 150 °C for 15 h. On cooling the mixture was mixed with DCM (50 mL) and extracted with  $\text{H}_2\text{O}$  (50 mL), then dried over  $\text{MgSO}_4$ , concentrated under reduced pressure and purified by chromatography on silica gel. Elution with ether:light petroleum ether 40–60 (25:75) gave the title compound (621 mg, 62%), as golden plates, m.p. 168–169 °C (from ether/light petroleum ether 40–60).  $\lambda_{\text{max}}$  ( $\text{CH}_2\text{Cl}_2$ )/nm 384 (log  $\epsilon$  4.08) and 281 (3.97);  $\nu_{\text{max}}$  (KBr disc) 3316s, 1618s, 1592s, 1577s, 1504s, 1493s, 1408w, 1323s, 1271s, 1215s, 1139vs, 816s, 746s, 695s, 687s, 639m, 613m, 587s, 566s, 545s, 501s and 452s;  $\delta_{\text{H}}$ (400 MHz;  $\text{CDCl}_3$ ) 4.27 (2H, s), 4.8–5.1 (1H, s, br), 6.09 (1H, s), 7.10 (2H, d,  $J=7.6$ ), 7.17 (1H, t,  $J=7.4$ ), 7.22 (2H, d,  $J=7.2$ ), 7.27–7.34 (6H, m), 8.06 (1H, d,  $J=8.4$ ) and 9.97 (1H, s);  $\delta_{\text{C}}$ (100.1 MHz;  $\text{CDCl}_3$ ) 47.3, 93.3, 106.1, 124.4, 125.2, 127.2, 127.7, 128.9, 129.1, 129.5, 137.4, 138.8, 145.9 and 153.7 (one peak is missing);  $m/z$  (orbitrap ASAP) 320.1391 ( $\text{M}^+\text{H}$ , 100%)  $\text{C}_{19}\text{H}_{18}\text{N}_3\text{O}_2$  requires 320.1394.

**2,4-Bis(butylamino)nitrobenzene (8):** 2,4-Difluoronitrobenzene (0.5 g, 3.14 mmol) and butylamine (1.0 mL) in EtOH (8 mL) were sealed in a Teflon-lined Parr bomb and heated at 150 °C for 15 h. On cooling, the mixture was mixed with DCM (50 mL), extracted with  $\text{H}_2\text{O}$  (50 mL), then dried over  $\text{MgSO}_4$ , concentrated under reduced pressure and purified by chromatography on silica gel. Elution with ether:light petroleum ether 40–60 (25:75) gave the title compound (757 mg, 84%) as a yellow solid, m.p. 58–59 °C (from ether/light petroleum ether 40–60).  $\lambda_{\text{max}}$  (EtOH)/nm 409 (log  $\epsilon$  4.19) and 268 (3.33);  $\nu_{\text{max}}$  (KBr disc) 3316w, 2860w, 2956w, 2929w, 1616vs, 1579s, 1543s, 1460m, 1399m, 1252vs, 1165vs, 1129vs, 819vs, 786m, 750s, 669m, 651m, 589s and 561s;  $\delta_{\text{H}}$ (400 MHz;  $\text{CDCl}_3$ ) 0.66–0.71 (6H, m), 1.12–1.21 (4H, m), 1.31–1.45 (4H, m), 2.89 (2H, t,  $J=7.2$  and 7.2), 2.94 (2H, t,  $J=7.2$  and 7.2), 4.30–4.70 (1H, s, br), 5.35 (1H, d,  $J=2.0$ ), 5.64 (1H, dd,  $J=9.2$  and 2.4), 7.70 (1H, d,  $J=9.6$ ) and 8.25 (1H, s, br);  $\delta_{\text{C}}$ (100.1 MHz;  $\text{CDCl}_3$ ) 13.8, 20.2, 20.3, 30.8, 31.0, 42.6, 43.0, 89.9, 105.1, 123.4, 129.1, 148.7 and 154.5 (one methyl group is missing);  $m/z$  (orbitrap ASAP) 266.1863 ( $\text{M}^+\text{H}$ , 100%),  $\text{C}_{14}\text{H}_{24}\text{N}_3\text{O}_2$  requires 266.1863.

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