An Organic Zeolite With 10 Å Diameter Pores Assembles From a Soluble and Flexible Building Block by Non-Covalent Interactions

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Two similar molecular building blocks, which both contain a hydrogen-bonded nitro group, have been prepared and crystallised. One structure has more flexibility with a butyl side chain which allows an open framework organic zeolite to form with large 10 Å diameter pores, whereas the other structure has less flexibility with an aryl side chain and is close packed. The pore size is comparable with those of the aluminophosphate VPI-5 (12 Å). It is concluded that some flexibility in the design of the building block for porous organic molecular materials was beneficial.

1. Introduction

Recently we reported the crystal structures of cyclic hexameric motifs formed from 2,4-bis(phenylamino) nitrobenzene **1** or 2,4-bis(butylamino)nitrobenzene **2** in which adjacent molecules are linked by N—H—O hydrogen bonds (Figure 1).[1–2] The hexamers formed from 2,4-bis(phenylamino)nitrobenzene **1** are stacked on top of each other so that large channels arise but the hexamers formed from 2,4-bis(butylamino)nitrobenzene **2** have a staggered stacking arrangement so that channels do not occur in the crystal. The open framework formed from compound **1** is an example of a nanoporous material comprised of discrete organic molecules between which there are only weak non-covalent interactions. This is quite rare as most organic molecules pack to minimise the void volume.[3] In contrast there are many examples of metal-organic frameworks (MOF's) which have porosity.[4–13]

Organic crystals which form channels have been referred to as 'organic zeolites' owing to their structural similarity to inorganic ones.[14] Inorganic zeolites have many applications such as molecular separation, heterogeneous catalysis, hydrogen storage and carbon dioxide capture.[15–20] The soluble precursors required for organic zeolites may include and extend the range of these applications because of solution processing, the choice of components and their functionality (Figure 2).[3] Tris-(o-phenylenedioxy)cyclotriphosphazene **3** forms crystals with empty 1D channels, 5 Å in diameter, that can clathrate solvent and organic guest molecules.[21–22] Dipeptides such as compound **4** crystallise with hydrogen bonded tubular assemblies forming 1D channels with diameters of 3–5.4 Å. These

channels were filled with solvent that could be evacuated by heating.[23–24] Cyclic host **5** forms cylindrical channels 5–8 Å in diameter stabilised by urea-urea hydrogen bonding and aromatic stacking.[25–26] The material was able to absorb carbon dioxide. 1,2-Dimethoxy-p-tert-butylcalix[4]dihydroquinone **6** crystallises in a tubular fashion to form two types of void space filled with water molecules. One void space is a 3D network of channels with diameters of 3.9 and 8.5 Å and the other void space consists of spherical cages of 11.2 Å in diameter connected by narrow channels.[27–28] The host retained its structural integrity upon removal of the water molecules. 3,3'-4,4'-Tetra(trimethylsilylethynyl)biphenyl **7** crystallises forming narrow channels in three dimensions that interconnect large internal voids of diameter 11 Å.[29] The porosity of the desolvated crystals was shown by nitrogen and hydrogen absorption.

2. Results and Discussion

Owing to the crystallisation of novel hydrogen bonded macrocyles from 2,4-bis(phenylamino)nitrobenzene **1** and from 2,4-bis(butylamino)nitrobenzene **2** (Figure 1) we wanted to synthesise more complex oligomeric scaffolds to investigate their molecular frameworks with a view to discovering organic zeolites that possess large channels with tailored pore sizes because of the diverse derivatization chemistry that is possible. Two compounds were made for comparison, Figures 3 and 4. The first step involves coupling a primary amine, butylamine or aniline, to give intermediates **9** and **12** respectively. These can be isolated but it was found convenient to generate them in situ and react them with 1,4-diaminobutane **10** to give compounds **11** and **13** respectively. Both compounds were successfully crystallised and the structures were solved by X-ray single crystal structure determinations.

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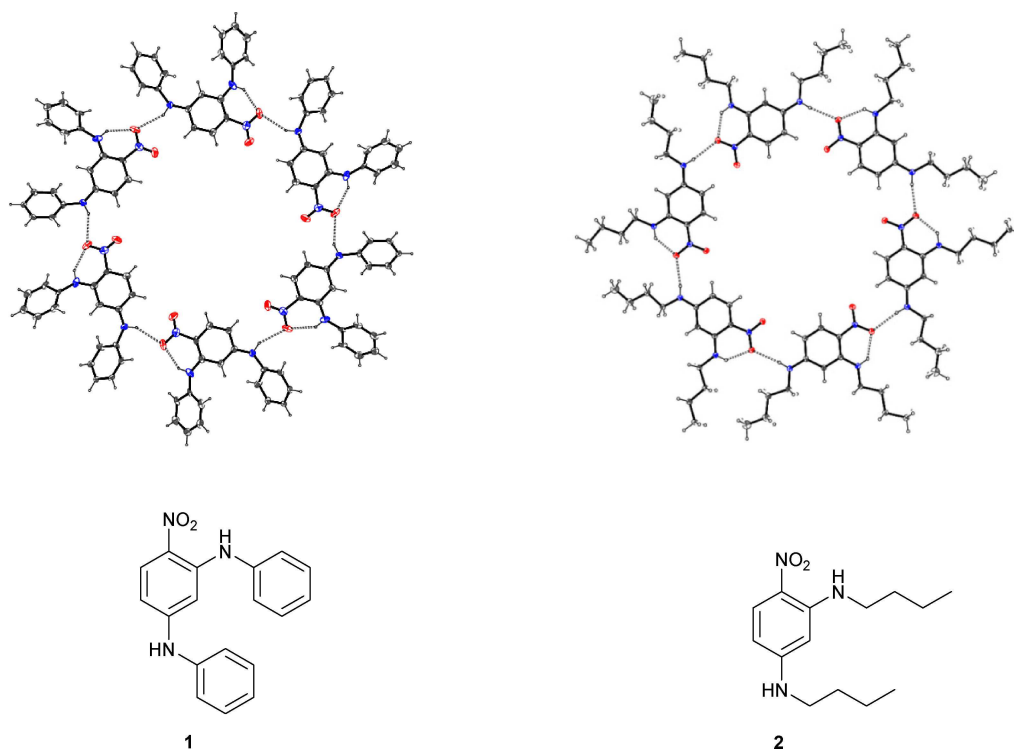E-mail: m.j.plater@abdn.ac.uk

Figure 1. Two examples of hydrogen-bonded hexamers crystallised from 2,4-bis(phenylamino)nitrobenzene **1** and 2,4-bis(butylamino)nitrobenzene **2**
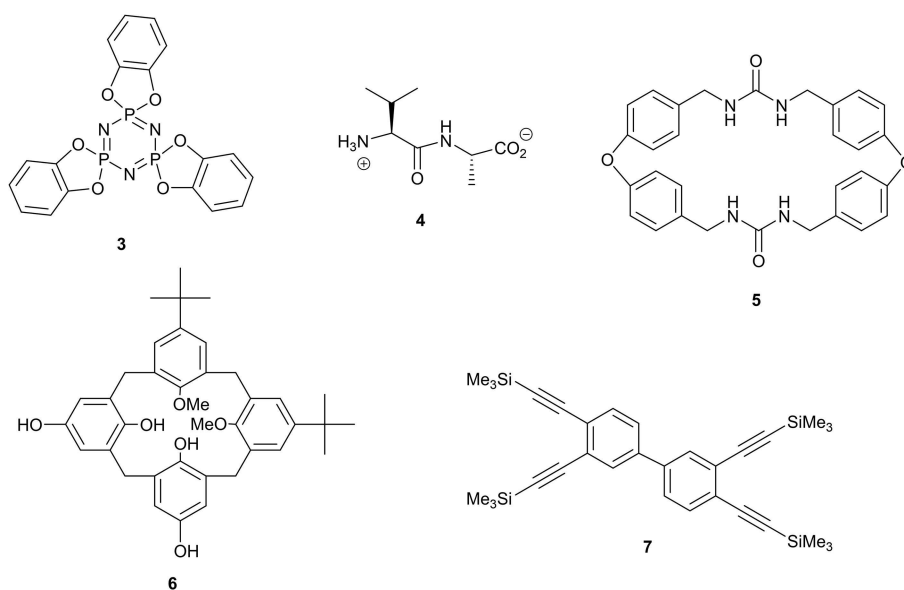

Figure 2. Some examples of 'organic zeolites' that crystallise possessing open channels.

2.1. The Crystal Structure of Compound 11

Compound **11** crystallises with one molecule in the asymmetric unit (Figure 5) in which the dihedral angle between the C1–C6 and C11–C16 aromatic rings is 37.91 (6)°. The chain linking these rings is characterised by torsion angle of C4–N1–C7–C8 = −167.0 (2), N1–C7–C8–C9 = 53.6 (3), C7–C8–C9–C10 = 166.5 (2), C8–C9–C10–N4 = 61.8 (3) and C9–C10–N4–C11 = 86.8 (3)°. The

nitro groups are almost coplanar with their attached rings [dihedral angle for N5/O1/O2 + C1–C6 = 2.2 (4)°; N6/O3/O4 + C11–C16 = 3.0 (3)°]. These geometries are consolidated by intra-molecular N2–H2···O1 and N3–H3a···O3 hydrogen bonds. The N2-bonded butyl side chain has an extended geometry whereas the N3-bonded chain features disorder of the final methylene group and methyl group over two sets of sites in a 0.509 (7):0.491 (7)
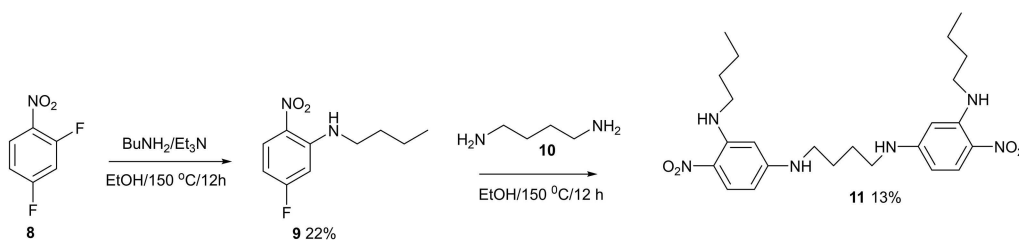
Figure 3. The synthesis of building block **11**. The molecular structure was shown, by an X-Ray single crystal structure determination, to be a porous organic zeolite.
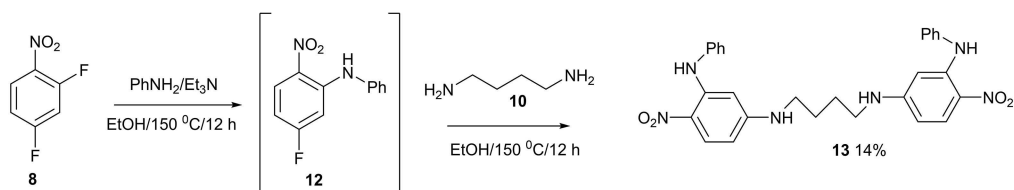

Figure 4. The synthesis of building block **13** which was crystallised and the molecular structure determined to be close packed by an X-Ray single crystal structure determination.
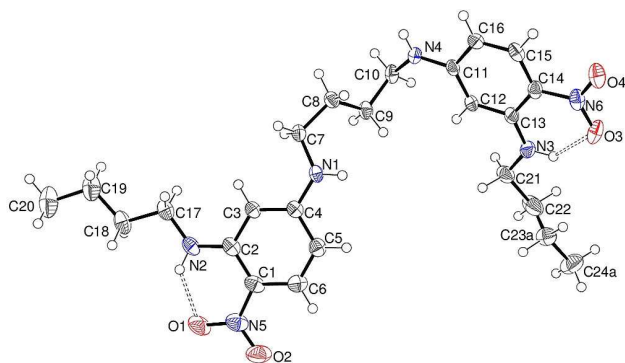

Figure 5. The molecular structure of compound **11** from an X-Ray single crystal structure determination showing 50% displacement ellipsoids with hydrogen bonds indicated by double-dashed lines.

ratio. Otherwise, the bond lengths and angles in structure **11** are unexceptional.

In the crystal structure of compound **11**, the *para* NH groups in the linking chain are key to constructing the supramolecular network. The N1–H1 group links to O4 (H···O = 2.26 Å) in an adjacent molecule generated by crystallographic inversion symmetry to form an $R_2^2(26)$ loop. The N4–H4 moiety forms an asymmetric, bifurcated hydrogen bond to O1 (H···O = 2.18 Å) and O2 (H···O = 2.52 Å) in an adjacent molecule to generate a hexameric ring (Figure 6) with an $R_6^6(78)$ graph-set *motif*. This resembles the hydrogen-bonded hexamer in 2,4-bis(butylamino) nitrobenzene **2**[1] shown in Figure 1 above with the important difference that the *ortho* N-butyl chain in compound **11** is oriented towards the centre of the hexamer rather than pointing away from it. The symmetry of the hexameric assembly is $\bar{3}$ about the point (1, 0, $^1/_2$) for the asymmetric molecule and its five clones. Taken together, the N1 and N4 hydrogen bonds link the molecules into 'honeycomb' (001) sheets. When the sheets are stacked in the *c*-direction in space group $R\bar{3}$, the pores overlap and generate a

nanoporous one-dimensional [001] channel system (Figure 7). The channel walls, 10 Å in diameter, consists of the methylene and methyl groups of the C17–C20 butyl side chains and are presumably strongly hydrophobic. A PLATON[30] analysis of the structure showed that some 2660 Å^3 per unit cell, 20% of the unit-cell volume, is solvent accessible 'empty space.' This may be compared to the volume of a molecule of H$_2$ in the liquid state of about 50 Å^3. The pore size is comparable to that of the aluminophosphate VPI-5 (12 Å)[20]

2.2. The Crystal Structure of Compound 13

Compound **13** crystallises with two molecules (containing C1 and C29) in the asymmetric unit with generally similar conformations, which approximate overall to S shapes: the C1 molecule is illustrated in Figure 8. The dihedral angles between the nitrobenzene rings in the C1 and C29 molecules are 18.26 (19)° and 14.2 (2)° respectively. The linking chains in each molecule feature *gauche* conformations for both the C$_{ar}$–N–C$_m$–C$_m$ (ar = aromatic, m = methylene) groupings and near *anti* conformations for the others. Each molecule features two intramolecular N–H···O hydrogen bonds from the *ortho*-NH group to one of the nitro O atoms, as also seen in compound **11**. Further similarities are seen in terms of the dihedral angles between the nitrobenzene rings and their pendant phenyl groups: 49.56 (15)° and 47.19 (14)° for the C1 molecule and 44.78 (14)° and 49.65 (13)° for the C29 molecule. Otherwise, the bond lengths and angles in compound **13** may be regarded as normal.

The packing for compound **13** is largely determined by hydrogen bonds to nitro group oxygen atoms arising from the *para* NH groups. Rather than inversion dimers and hexamers as seen in compound **11**, the N–H···O hydrogen bonds in compound **13** lead to tetrameric $R_4^4(32)$ loops (Figure 9) as components of two separate (for the C1 and C29 molecules)
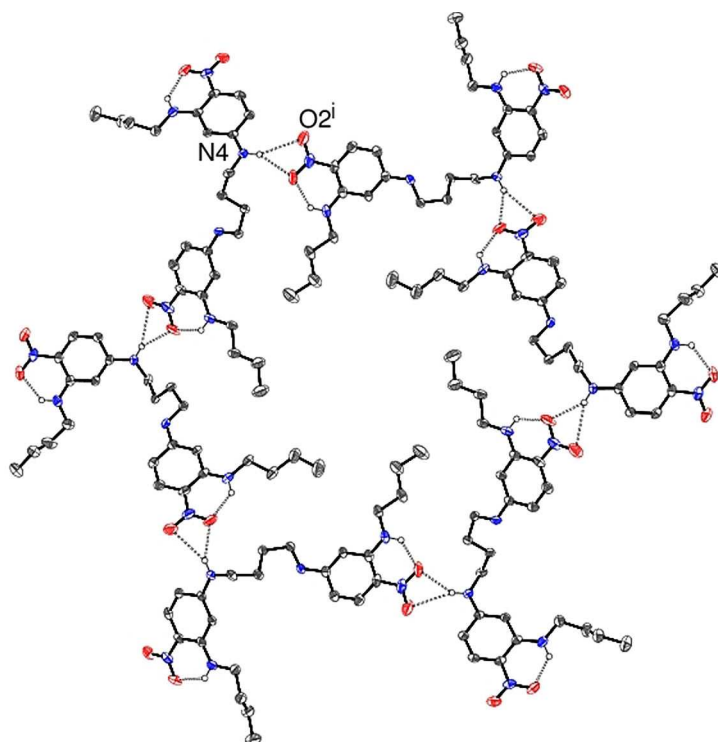
Figure 6. A hydrogen-bonded hexamer in the organic zeolite framework of compound **11** arising from cooperative N4–H4·· (O1,O2) links; symmetry code (i) =1+y, 1−x+y, 1−z. The butyl side chains pack together forming channels which are 10 Å in diameter.
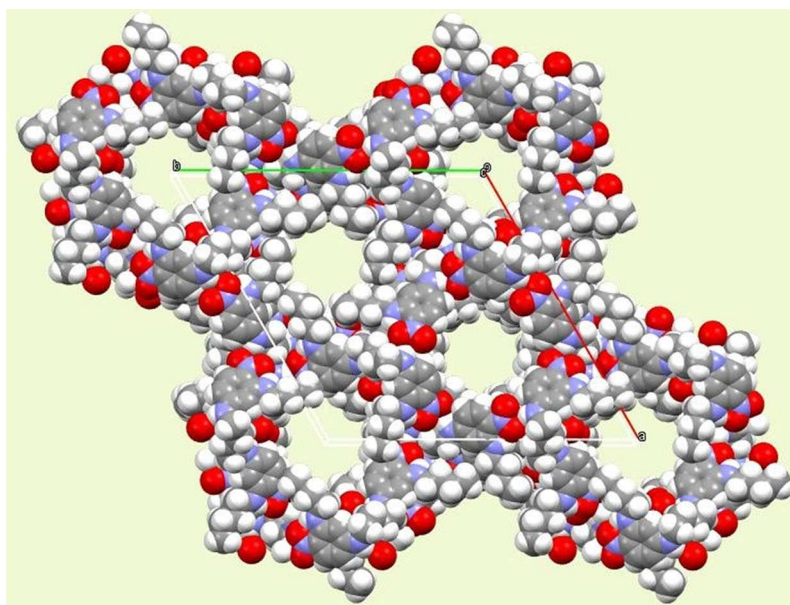

Figure 7. Space-filling representation of the packing in the organic zeolite framework of compound **11** showing the formation of 10 Å diameter [001] channels centred at x=0, y=0 and equivalent locations according to rhombohedral crystal symmetry. The channels are of comparable size to those of the aluminophosphate VPI-5 (12 Å)[20]

infinite sheets, which both propagate in the (101) plane. No pores or channels can be identified and PLATON did not reveal any free space, so the packing may be described as 'dense', which is reflected in the much higher density in compound **13** (1.370 g cm^{-3}) compared to compound **11** (1.049 g cm^{-3}).

3. Conclusions

An organic zeolite has been crystallised which possesses large channels 10 Å in diameter. These are large compared to those which occur in typical organic zeolites described in the
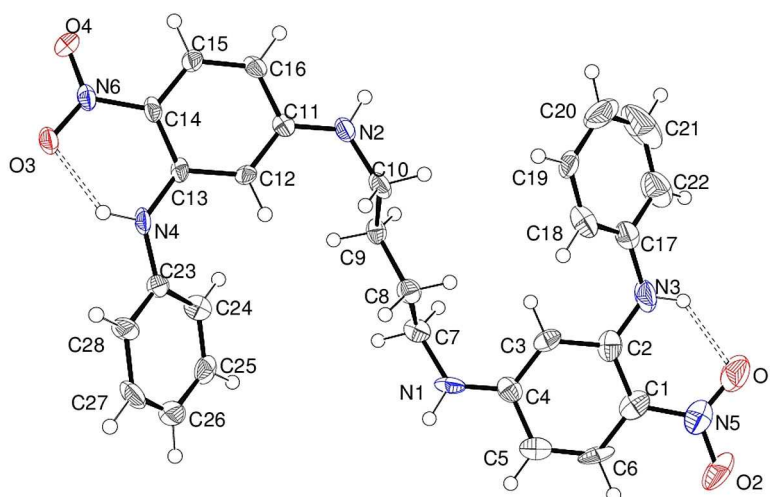
Figure 8. The close packed structure of the C1 molecule in compound **13**, from an X-Ray single crystal structure determination, showing 50% displacement ellipsoids with hydrogen bonds indicated by double-dashed lines.
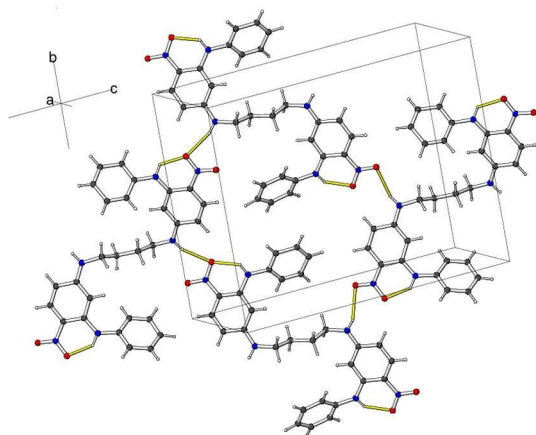

Figure 9. The close packed structure of compound **13** showing the formation of tetrameric assemblies as components of (101) infinite hydrogen bonded sheets.

introduction[3] and were formed using a flexible, rather than a rigid, building block. They are similar in size to those of some inorganic zeolites such as the aluminophosphate VPI-5.[20] The pores are formed by the close packing of butyl side chains which leaves a large hole in the center. In contrast replacement of the butyl side chains with aryl rings changes the packing mode into a close packed structure with no channels. This work suggests that some flexibility in organic molecular building blocks may allow packing which favours open channel frameworks[12] and that a wider range of functional groups, such as the nitro group, can be used. In this work building blocks with steric bulk can favour crystallisation of a cyclic hexameric motif, rather than an extended array, that leads to a porous solid. An anology is provided in solution assembly where steric bulk favours cyclic 'rosettes' rather than extended 'crinkled tape' motifs.[31] Also, in a broader context for the future, oligomeric building blocks may be designed and extended by iterative synthesis to cell membrane dimensions and molecular

design may lead to tailored pores of increasing diameter and stability with many applications.[20]

Experimental

General: IR spectra were recorded on a diamond anvil spectrophotometer. UV spectra were recorded using a Perkin-Elmer Lambda 25 UV-VIS spectrometer with EtOH as the solvent. ^{1}H and ^{13}C NMR spectra were recorded at 600 MHz and 150 MHz, respectively, using a Varian 400 spectrometer. Chemical shifts, δ are given in ppm relative to the residual solvent and 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. Compound **12** has been reported previously.[1]

N-Butyl-5-fluoro-2-nitroaniline 9

2,4-Difluoronitrobenzene **8** (500 mg, 3.14 mmol), butylamine (230 mg, 3.15 mmol) and an excess of triethylamine (700 mg, 6.93 mmol) were mixed in EtOH (20 ml) and heated at 150 °C for 12 h. After cooling the mixture was diluted with water (150 ml) and acidified with cHCl (2 ml). The mixture was then extracted with CH_2Cl_2 (100 ml×2) and the combined extracts were back extracted with water (100 ml) followed by drying with $MgSO_4$ and filtration. The filtrate was evaporated *in vacuo* and purified by chromatography on silica gel. Elution with dichloromethane gave the *title compound* (147 mg, 22%) as a yellow oil which crystallised on scratching, m.p. 37–38 °C (from ether/light petroleum ether 40–60); ^{1}H NMR (600 MHz; CDCl$_3$, 25 °C): δ = 7.92 (t, ^3J(H,H) = 12 and 6 Hz, 1H), 7.89 (s, 1H), 6.21 (d, J(H,H) = 12 Hz, 1H), 6.07 (t, ^3J(H,H) = 12 and 6 Hz, 1H), 2.96-3.02 (m, 2H), 1.43–1.50 (m, 2H), 1.19–1.27 (m, 2H), 0.73 (t, ^3J(H,H) = 6 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$, 25 °C): δ = 168.3, 166.8, 147.5, 129.9, 103.8, 99.4, 99.0, 43.0, 30.7, 20.2, 13.7; IR (Diamond): 526, 576, 748, 827, 993, 1056, 1214, 1249, 1509, 1572, 1627, 2863, 2937, 2963, 3380 cm^{-1}; UV/Vis (EtOH): λ_{max} (ε) = 409 (50,118), 229 (50,118 mol^{-1}dm^3 cm^{-1}); HRMS (Orbitrap ASAP): *m/z* calcd for C$_{10}$H$_{13}$FN$_2$O$_2$: 213.1039 [M$^+$ + H]; found: 213.1038.

$N^1,N^{1'}$-(Butane-1,4-diyl)bis (N^3-butyl-4-nitrobenzene-1,3-diamine) 11

2,4-Difluoronitrobenzene **8** (500 mg, 3.14 mmol), butylamine (230 mg, 3.15 mmol) and an excess of triethylamine (700 mg, 6.93 mmol) were mixed in EtOH (20 ml) and heated at 150 °C for 12 h. The mixture was allowed to cool and 1,4-diaminobutane **10** (138 mg, 1.57 mmol) was added. The mixture was heated for a further 12 h at 150 °C. After cooling the mixture was diluted with water (150 ml) and acidified with cHCl (2 ml). The mixture was then extracted with CH_2Cl_2 (100 ml×2) and the combined extracts were back extracted with water (100 ml) followed by drying with $MgSO_4$ and filtration. The filtrate was evaporated *in vacuo* and purified by chromatography on silica gel. Dichloromethane elutes by-products then elution with an ether/dichloromethane mixture (20:80) gave the title compound (105 mg, 13%) as a yellow solid, m.p. 124–125 °C (from ether/light petroleum ether 40–60); ^1H NMR (600 MHz; $CDCl_3$, 25 °C): $\delta = 8.52$ (s, 2H), 7.98 (d, J(H,H) = 12 Hz, 2H), 5.92 (d, J (H,H) = 12 Hz, 2H),), 5.63 (s, 2H), 3.19–3.29 (m, 8H), 1.81–1.83 (m, 4H), 1.68–1.74 (m 4H), 1.43–1.52 (m, 4H), 0.95–0.99 (t, ^3J(H,H) = 12 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): $\delta = 154.5$, 148.8, 129.2, 123.6, 104.8, 89.9. 42.8, 42.5, 30.9, 26.6, 20.4, 13.9; IR (Diamond): 548, 749, 799, 1160, 1257, 1406, 1466, 1572, 1612, 2861, 2928, 2954, 3331 cm^{-1}; UV/Vis (EtOH): λ_{max} (ε) = 406 (19,952), 234 (50,118 mol^{-1}dm^{3}cm^{-1}); HRMS (Orbitrap ASAP): *m/z* calcd for $C_{24}H_{36}N_6O_4$: 473.2876 [M$^+$ +H]; found: 473.2880 .

$N^1,N^{1'}$-(Butane-1,4-diyl)bis (4-nitro-N^3-phenylbenzene-1,3-diamine) 13

2,4-Difluoronitrobenzene **8** (500 mg, 3.14 mmol), aniline (292 mg, 3.14 mmol) and an excess of triethylamine (700 mg, 6.93 mmol) were mixed in EtOH (20 ml) and heated at 150 °C for 12 h. The mixture was allowed to cool and 1,4-diaminobutane **10** (138 mg, 1.57 mmol) was added. The mixture was heated for a further 12 h at 150 °C. After cooling the mixture was diluted with water (150 ml) and acidified with cHCl (2 ml). The mixture was then extracted with CH_2Cl_2 (100 ml×2) and the combined extracts were back extracted with water (100 ml) followed by drying with $MgSO_4$ and filtration. The filtrate was evaporated in vacuo and purified by chromatography on silica gel. Dichloromethane elutes by-products then the title compound (115 mg, 14%) as a yellow solid, m.p. 176–178 °C (from ether/light petroleum ether 40–60); ^1H NMR (600 MHz; $CDCl_3$, 25 °C): $\delta = 9.95$ (2H, s), 8.09 (2H, d, J = 12.0), 7.39-7.43 (4H, m), 7.30–7.32 (4H, m), 7.21–7.24 (2H, m), 6.08 (2H, s), 6.00 (2H, d, J = 12.0), 3.07–3.10 (4H, m), 1.60–1.63 (4H, m); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): $\delta = 165.6$, 154.0, 147.6, 138.9, 129.6, 129.3, 125.6, 124.7, 104.7, 96.0, 42.7, 26.5; IR (Diamond): 491, 689, 751, 818, 1101, 1215, 1259, 1323, 1468, 1495, 1520, 1540, 1574, 1587, 1615, 2865, 2941, 3323 cm^{-1}; UV/Vis (EtOH): λ_{max} (ε) = 408 (19,952), 276 (7,943), 225 (15,849 mol^{-1}dm^{3}cm^{-1}); HRMS (Orbitrap ASAP): *m/z* calcd for $C_{28}H_{28}N_6O_4$: 513.2250 [M$^+$ +H]; found: 513.2254.

Crystal Structure Determinations

Crystals of compounds **11** and **13** were recrystallized from dichloromethane/light petroleum ether solution and intensity data were collected at $T = 100$ K using a Rigaku AFC12 area-detector diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å). The structures were solved by direct methods and completed and optimised by refinement against $|F|^2$ with SHELXL-2014.[32] The H atoms were positioned geometrically (N–H = 0.88 Å, C–H = 0.95–0.99 Å) and refined as riding atoms with the constraint $U_{iso}(H) = 1.2U_{eq}$(carrier) or 1.5U_{eq}(methyl carrier) applied in all cases. One of the butyl side chains in compound **11** was modelled as being disordered over two sets of sites. The [001] channels in compound **11** may contain

highly-disordered solvent molecules but these could not be modelled and the crystal data below only refer to the main molecule. The crystal of compound **13** chosen for data collection was found to be a non-merohedral twin with the components related by a rotation of 180° about [001] in real space; the domain fractions refined to 0.5339 (8): 0.4661 (8).

11 $C_{24}H_{36}N_6O_4$, $M_r = 472.59$, light-orange needle, 0.30×0.03×0.03 mm, trigonal, space group $R\bar{3}$ (No. 148), $a = 32.1022$ (10) Å, $c = 15.0899$ (5) Å, $V = 13467.5$ (10) Å^3, $Z = 18$, $\mu = 0.073$ mm^{-1}, $\rho_{calc} = 1.049$ g cm^{-3}, 30466 data scanned ($2\theta_{max} = 51°$), $R_{int} = 0.035$, $R(F) = 0.080$ [4414 merged reflections with $I > 2\sigma(I)$], $wR(F^2) = 0.263$ (5569 merged reflections), CCDC deposition number 1887584.

13 $C_{28}H_{28}N_6O_4$, $M_r = 512.56$, yellow slab, 0.20×0.04×0.02 mm, monoclinic, space group $P2_1$ (No. 4), $a = 8.1538$ (4) Å, $b = 15.5507$ (6) Å, $c = 19.6185$ (8) Å, $\beta = 92.247$ (4)°, $V = 2485.66$ (18) Å^3, $Z = 4$, $\mu = 0.094$ mm^{-1}, $\rho_{calc} = 1.370$ g cm^{-3}, 12320 data scanned from two twin components ($2\theta_{max} = 52°$), $R(F) = 0.064$ [9234 reflections with $I > 2\sigma(I)$], $wR(F^2) = 0.134$ (12320 reflections), absolute structure indeterminate, CCDC deposition number 1887585.

Conflict of Interest

The authors declare no conflict of interest.

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