Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 3701–3707

TETRAHEDRON

Syntheses and X-ray crystal structures of poly(pyridylsulfanylmethyl)arenes: new multi-armed molecules

David A. McMorran* and Peter J. Steel

Department of Chemistry, University of Canterbury, Christchurch, New Zealand

Received 3 January 2003; revised 25 March 2003; accepted 4 April 2003

Abstract—The synthesis of a series of seven new poly(pyridylsulfanylmethyl)arenes is reported. These are readily prepared from either 2- or 4-mercaptopyridine and a poly(bromomethyl)arene in the presence of triethylamine. Compounds with three, four, six and eight pyridylsulfanylmethyl arms are reported. These have been fully characterised and, in four cases, the relative orientations of the pyridylsulfanylmethyl arms have been ascertained by X-ray structural analysis.

1. Introduction

Over recent years there have been an increasing number of reports of so-called 'multi-armed' molecules. This term describes molecules in which a core unit, most often an aromatic ring(s), is appended by a number of long, semi-rigid or flexible, aromatic and/or aliphatic chains (the 'arms'). The number of arms depends on the nature of the core unit: for example, a benzene core unit can accommodate up to six arms. While such molecules can be synthetically challenging, as there may be considerable steric resistance to attaching, for example, six arms around a benzene ring, an increasing number of multi-armed molecules are appearing in the literature, often with names reflecting the shapes, e.g. asterisk molecules,[1] octopus ligands,[2] and spider hosts.[3]

Such molecules are of interest in a range of contexts. For example, multi-armed molecules, in which an aromatic core is appended by long aliphatic arms, find uses as discotic liquid crystals.[4] In particular, triphenylene, appended by six arms, is becoming widely used as a core in such molecules.[5] Benzene cores appended by six flexible arms, each terminated by an anionic group, have recently been shown to form micelles in aqueous solutions.[1] Other systems containing naphthalene core units have been shown to act as hosts for a range of solvent molecules.[3] Multi-armed arenes have also been frequently used as core units for dendrimers.[6] To a lesser extent, multi-armed molecules, in which the arms contain suitable donor functionalities, have been used as ligands for metal ions.[7] The manner in which they can do this is determined by the nature, and number, of the donor groups built into the arms, the number and relative arrangement of the arms about the core unit, and by the electronic and structural requirements of the metal ion in question.

An important consideration in the design of such compounds is how the arms will arrange themselves about the core unit. Various studies have shown that the most favoured arrangement, on steric grounds, is one where all adjacent arms are on opposite sides of the plane of the core unit,[8,9] and this pre-organisation of the arms has been utilized by a number of groups.[10]

We report here the preparation and characterisation of a series of new multi-armed molecules, which we have prepared as a part of our studies into the effects on metal ion coordination of incorporating flexibility into poly-heterocyclic N-donor ligands.[11] The new molecules each contain an arene core, to which are appended three, four, six or eight pyridylsulfanylmethyl arms, and are shown in Figure 1.[12,13] Compound **8** represents a rare example of a multi-armed molecule incorporating a biphenylene core platform.

We also report here the X-ray crystal structures of four of these compounds, namely 1,3,5-tris(2-pyridylsulfanylmethyl)-2,4,6-trimethylbenzene (**1**), 1,2,4,5-tetrakis(2-pyridylsulfanylmethyl)benzene (**3**), hexakis(4-pyridylsulfanylmethyl)benzene (**7**) and octakis(2-pyridylsulfanylmethyl)biphenylene (**8**). These show that, in three of the four cases, the arms are arranged in the sterically preferred arrangement, i.e. alternating above and below the central arene platform, whereas in the case of **3**, the arms adopt a different arrangement in the solid state.

Keywords: multi-armed molecules; biphenylene; X-ray structures.

* Corresponding author. Tel.: +64-3-479-7934; fax: +64-3-476-7906; e-mail: davidm@alkali.otago.ac.nz

0040–4020/03/$ - see front matter
doi:10.1016/S0040-4020(03)00550-7

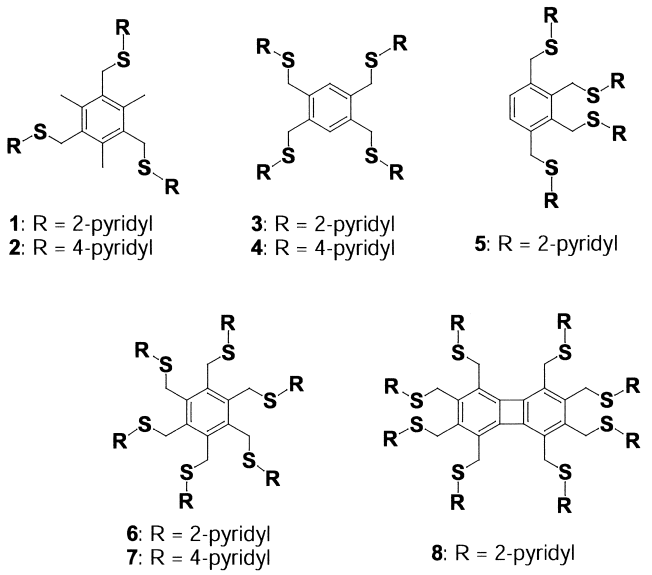


Figure 1.

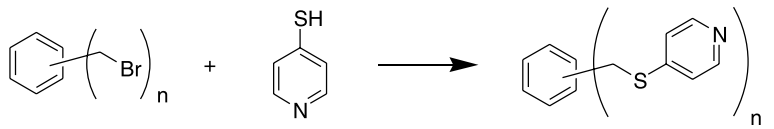
2. Results and discussion

The new compounds were prepared from the appropriate poly(bromomethyl)arene by treatment with either 2- or 4-mercaptopyridine and triethylamine in cold acetonitrile solution (Scheme 1). They were isolated as pale-coloured solids in moderate to good yields and their constitutions confirmed by microanalysis and by electrospray mass spectrometry of their protonated adducts. In each case, the 4-pyridyl isomer was much less soluble than the 2-pyridyl and, interestingly, the solubility of **3** was found to be much poorer than that of the less symmetrical isomer **5**.

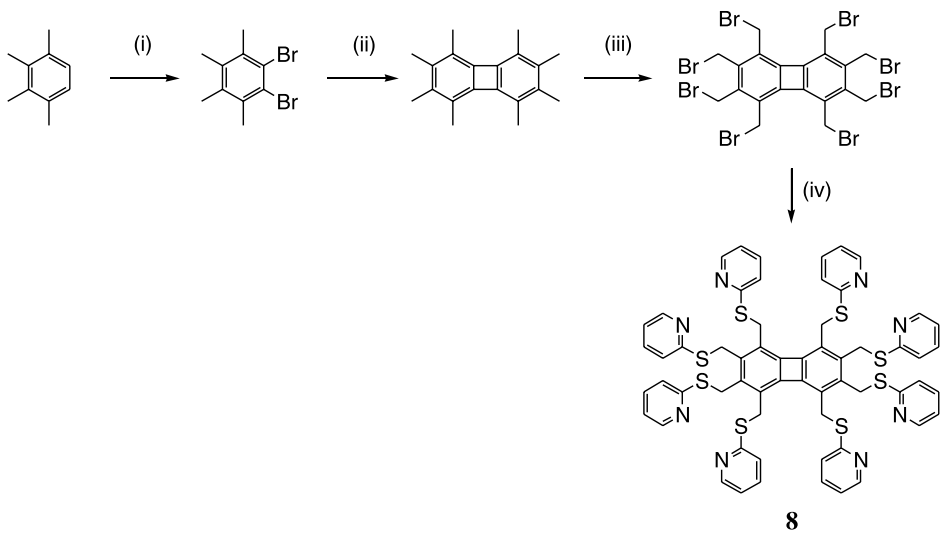
The compounds were also characterised by ^{1}H NMR spectroscopy, in either $CDCl_3$ or, where necessary, DMSO-d_6. Assignment of the pyridine ring protons was confirmed by 1-D TOCSY experiments. In the case of **5**, the ^{1}H NMR spectrum shows two sets of CH_2-pyridyl ring signals, due to the 'outer' (C_1 and C_4) and 'inner' (C_2 and C_3) arms. Assignment of these was achieved by a 1-D nOe experiment, where irradiation of the CH_2 peaks gave observable enhancements of their adjacent pyridine $H_{3'}$ peaks, whereas only irradiation of the CH_2 peak at 4.56 ppm gave an enhancement to the central benzene ring protons H_5 and H_6, showing that this peak corresponds to the methylene groups of the 'outer' arms.

The synthesis of **8** is outlined in Scheme 2. Prehnitene was dibrominated[14] and then treated with *n*-butyllithium in anhydrous THF to give octamethylbiphenylene.[15] A free-radical bromination of this using an excess of *N*-bromosuccinimide, in the presence of dibenzoyl peroxide, gave octakis(bromomethyl)biphenylene as a bright yellow solid. EI-MS and ^{1}H NMR spectra confirmed the presence of the desired product. Reaction of octakis(bromomethyl)biphenylene with 2-mercaptopyridine proceeded cleanly and the resulting solid could be purified by recrystallisation from chloroform–diethyl ether solutions. The ^{1}H NMR spectrum showed two sets of peaks, due to the 'inner' and 'outer' arms, as was observed for **5**. These were assigned by 1-D TOCSY experiments and by comparison of the peak positions with those for **5**: one set of peaks has almost the same positions in both cases, while each signal of the second set lies about 0.3 ppm upfield in the spectrum of **8**, compared to that of **5**.

The two sets of peaks whose positions are invariant are those which, in the spectrum of **5**, are assigned to the inner arms. As it is these which might be expected to enjoy the most similar environment in both **5** and **8**, we assign these in



Scheme 1.



Scheme 2. (i) Br_2, cat. I_2, CH_3COOH; (ii) Bu_nLi, THF, −80 °C–RT; (iii) NBS, $(PhCO)_2O_2$, CCl_4, *hν*, reflux; (iv) 2-pySH, Et_3N, MeCN, 0 °C–RT.

this way. The second set of peaks, which shift upfield in the case of **8**, are then assigned to the outer arms, which, in the case of **8**, lie adjacent not only to one of the inner arms, as in the case of **5**, but also now to one of the arms in the *peri* position. The proximity of this second arm may result in the pyridine rings of the two arms interacting via a π-stacking interaction, which would in turn explain the upfield shifts observed for the peaks. The X-ray crystallographic analysis of **8**, discussed below, supports this proposal.

Four of the compounds, **1**, **3**, **7** and **8** were structurally characterised by X-ray crystallography. The structures of the new multi-armed molecules are of interest because, in each case, there are a number of structural forms possible, depending on the relative arrangement of the arms. The most favoured arrangement, based on steric arguments, has the arms alternating above and below the central arene platform.[8] Studies on related compounds comprising multiple arms have shown that this is usually the observed arrangement in such species, although other arrangements can be found in, for example, metal complex adducts.[16]

Crystals of **1** suitable for X-ray analysis were obtained by diffusion of petroleum ether into a chloroform solution. Figure 2 shows a perspective view of the structure, which crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit contains a whole molecule of **1**. The arms all adopt an *anti* geometry about the CH_2–S bonds and are arranged about the central benzene ring in the less hindered *aba* orientation,[17] with the pyridine rings lying at angles of 80.3° (N11–C16), 93.1° (N31–C36) and 84.0° (N51–C56) to the central benzene ring.

The molecules pack in the crystal with the central benzene ring of one molecule forming a π-stacking interaction with a pyridine ring of an adjacent molecule (closest inter-ring distance 3.45 Å, angle between ring meanplanes 6.6°). The molecules further interact via a (weak) CH···N hydrogen bond between a pyridine nitrogen on one arm and an aromatic CH on an arm of an adjacent molecule (N···C 3.44 Å, N···H–C 172.7°).

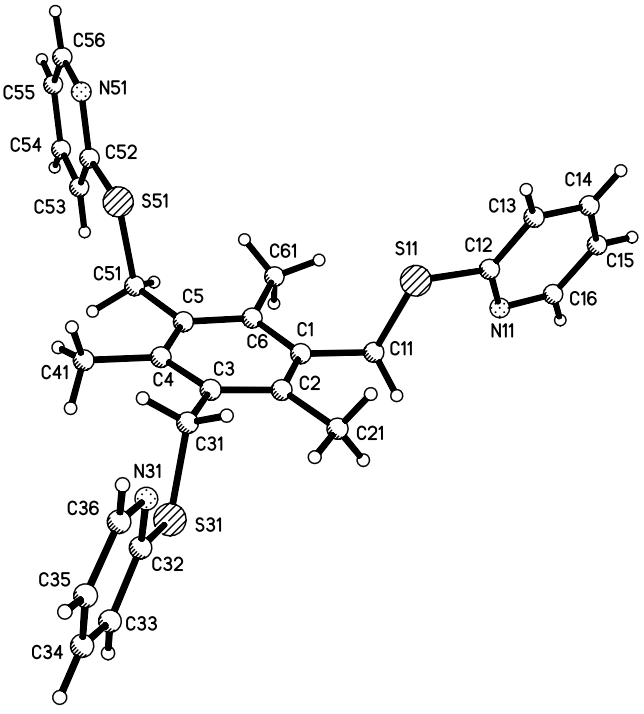


Figure 2. Perspective view of the structure of **1**, showing the crystallographic labeling.

Crystals of **3**, suitable for X-ray analysis, were obtained from an acetonitrile solution. Figure 3 shows a perspective view of the structure, which crystallizes in the triclinic space group *P*-1. The asymmetric unit contains half a molecule of **3** and a crystallographic centre of inversion lies at the centre of the benzene ring.

The arms, in this case, adopt an *abba* arrangement, with the pyridine rings lying at angles of 75.2° (N11–C16) and 76.1° (N21–C26) to the central benzene ring. Although adjacent arms lie on opposite sides of the central benzene ring, one of the arms adopts an *anti* conformation about the CH_2–S bond while the other arm has a *gauche* arrangement. This difference in orientation of the arms affects the intermolecular interactions between them. Consideration of the molecular packing shows that the rings that are involved in the *gauche* arrangement of the arms experience intermolecular π-stacking interactions, with a closest inter-ring distance of 3.59 Å. Surprisingly, there are no intermolecular hydrogen bonding interactions in this case.

Crystals of **7**, suitable for X-ray analysis, were obtained from a pyridine solution. Figure 4 shows a perspective view of the structure, which crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit contains half a molecule of **7** and half a diethyl ether solvate molecule. A crystallographic centre of inversion lies at the centre of the benzene ring. The arms all adopt an *anti* geometry about the CH_2–S bonds and are arranged about the central benzene ring in the sterically most favoured *ababab* orientation, with the pyridine rings lying almost orthogonal to the central benzene ring: the angles between the mean planes are 92.8° (N11–C16), 66.9° (N21–C26) and 85.1° (N31–C36).

Consideration of the molecular packing shows that the molecules are held together by a variety of intermolecular interactions. Two sets of hydrogen bonding interactions are present, between, in each case, a pyridine nitrogen and an aromatic CH group. The stronger of these has an N···C distance of 3.416 Å and an N···H–C angle of 168.3°. There are also strong π-stacking interactions between pyridine rings in adjacent molecules, with a closest intermolecular C···C distance of 3.37 Å. Finally, there are relatively strong intermolecular S···S interactions at a distance of 3.57 Å.[18] These interactions hold the molecules together in such a way as to generate channels, which run parallel to the *c* axis, within which the diethyl ether solvate molecules reside.

Crystals of **8**, suitable for X-ray analysis, were obtained by diffusing diethyl ether into a chloroform solution. Figure 5 shows a perspective view of the structure, which crystallizes in the orthorhombic space group *Ccca*. The asymmetric unit contains one quarter of a molecule of **8** and half a diethyl ether solvate molecule. Three mutually orthogonal two-fold rotation axes intersect at the centre of the central C_4 ring of the biphenylene core, generating the complete structure

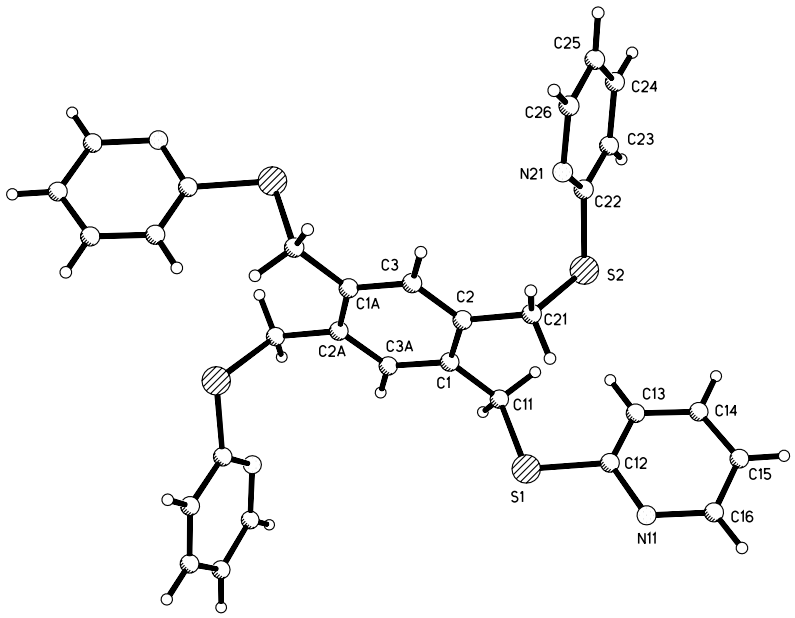


Figure 3. Perspective view of the structure of **3**, showing the crystallographic labeling.

with D_2 symmetry. The arms all adopt an *anti* geometry about the CH_2-S bonds and adopt the least hindered *abababab* arrangement about the central biphenylene core. The pyridine rings are almost orthogonal to the central biphenylene core, with angles between the mean planes of 87.8° (N21–C26) and 90.5° (N31–C36).

Despite lying on opposite sides of the biphenylene core, pairs of adjacent 'outer' arm pyridine rings experience intramolecular π-stacking interactions with each other, with a closest C···C distance of 3.60 Å. This provides good support for the justification of the ^{1}H NMR assignment of **8**, described above. The pattern of bond lengths and angles within the biphenylene core (Fig. 5) parallels those observed in other structurally characterised octa-substituted biphenylenes.[9,19] These have been interpreted to suggest that there is bond localisation in these molecules.[19,20]

Consideration of the molecular packing reveals columns, containing molecules of **8** and disordered diethyl ether solvate molecules alternately, which stack parallel to the *c* axis. These columns lie offset from each other, in a manner such that the 'inner' arms in adjacent columns interdigitate and form intermolecular hydrogen bonding interactions

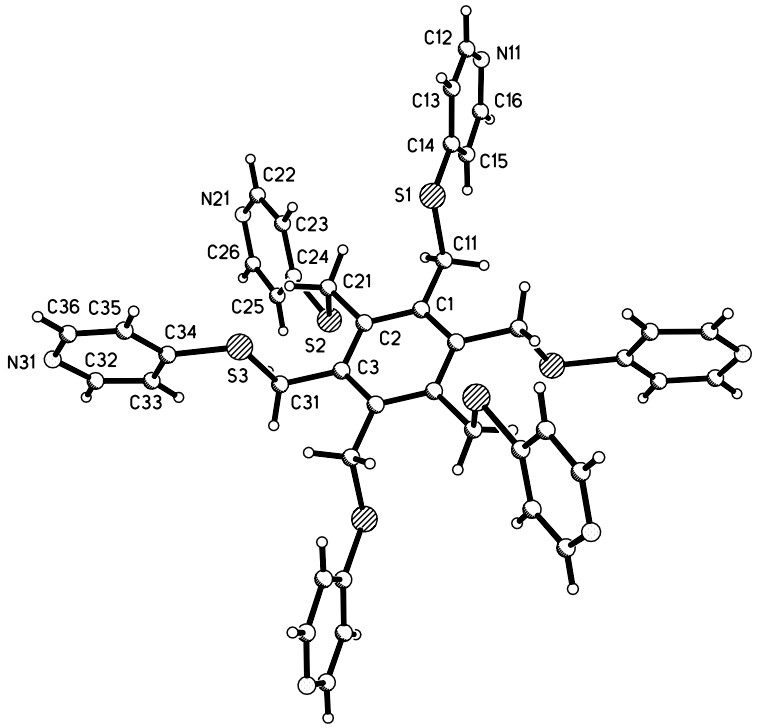


Figure 4. Perspective view of the structure of **7**, showing the crystallographic labeling. The diethyl ether solvate molecule is omitted for clarity.

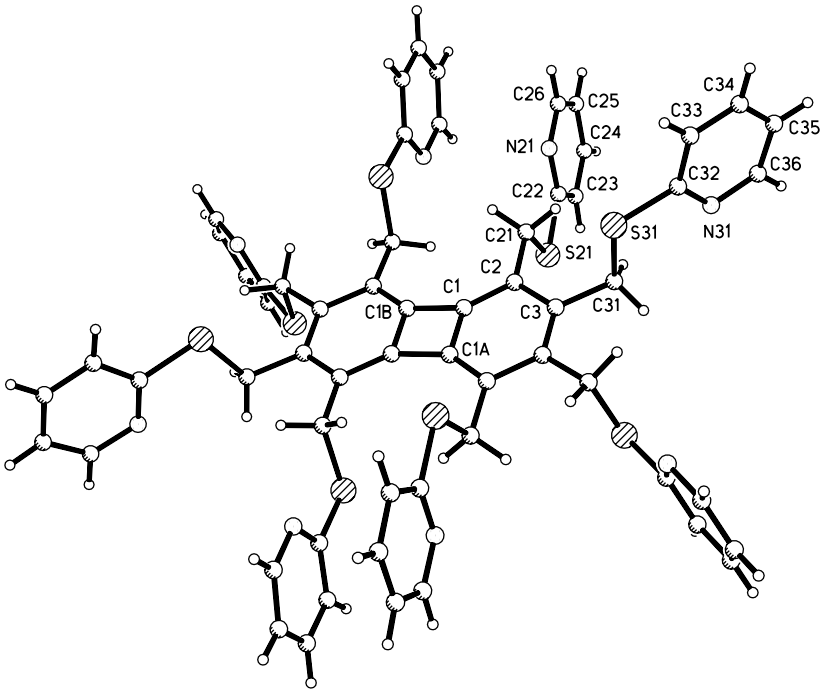


Figure 5. Perspective view of the structure of **8**, showing the crystallographic labeling. The diethyl ether solvate molecule is omitted for clarity. Selected bond lengths (Å) and angles (°). C1–C2 1.365 (3), C1–C1A 1.413 (4), C1–C1B 1.516 (4), C2–C3 1.438 (3), C1A–C1–C2 123.4 (1), C1–C2–C3 115.0 (2).

between pyridine nitrogens and aromatic CH units. All of the hydrogen bonds are the same and have an N···C distance of 3.549 Å and an N···H–C angle of 145.9°. The diethyl ether solvate, which lies in cavities formed between the two **8** molecules above and below it in the column and the **8** molecules which lie in the adjacent columns, are held in place by a number of O···H and S···H interactions.

This structure provides an interesting contrast to that of octaethylbiphenylene, the only other crystallographically characterised example of a multi-armed, biphenylene-cored molecule.[9] In this case, where the arms are substantially smaller than those in **8**, the molecule was found to adopt an *ababbaba* arrangement, with $C_{2\,h}$ symmetry, in the solid state. However, this was proposed to be due to crystal packing forces and the lower energy *abababab* arrangement was found in solution.

3. Experimental

3.1. General procedures

Compound **3** was prepared as described previously.[13] Octamethylbiphenyl,[15] 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene,[21] 1,2,4,5-tetrakis(bromomethyl)benzene,[22] 1,2,3,4-tetrakis(bromomethyl)benzene,[22] and hexakis-(bromomethyl)benzene[23] were prepared by literature procedures. 2- and 4-Mercaptopyridine were purchased from Aldrich and used as received. Melting points are uncorrected. NMR spectra were recorded on Varian 500 or 300 MHz NMR spectrometers. ES-MS spectra were recorded using a Micromass LCT TOF mass spectrometer. EI-MS spectra were recorded on a Kratos MS80RFA spectrometer. Elemental analyses were performed by the Campbell Microanalytical Laboratory at the University of Otago.

All the compounds were prepared in the same way. The preparation of **1** is given as a general procedure.

X-Ray crystallography. All measurements were made with a Siemens CCD area detector using graphite monochromatised Mo Kα (λ=0.71073 Å) radiation. Intensities were corrected for Lorentz and polarisation effects and for absorption. The structures were solved by direct methods using SHELXS,[24] and refined on F^2 using all data by full-matrix least-squares procedures with SHELXL-97.[25] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.3 times the isotropic equivalent of their carrier carbons. The functions minimised were $\Sigma w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + aP^2 + bP]^{-1}$, where $P = [\max(F_o)^2 + 2F_c^2]/3$.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC No. 194768, 194769, 194770 and 194771. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

3.1.1. Preparation of 1,3,5-tris(2-pyridylsulfanylmethyl)-2,4,6-trimethylbenzene (1). 1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene (1.78 g, 4.48 mmol) and 2-mercaptopyridine (1.49 g, 13.4 mmol) were stirred in acetonitrile (50 mL) at 0 °C. Triethylamine (1.69 g, 16.8 mmol) was added via syringe and the solution stirred overnight, slowly warming to room temperature. The resulting pale brown precipitate was filtered off, washed with water, acetonitrile and diethyl ether and dried. Recrystallization from hot acetonitrile gave **1** as a white crystalline solid. Yield: 1.41 g

(64%). Mp: 179–180 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 2.50 (s, 9H, CH_3), 4.50 (s, 6H, CH_2), 7.00 (dd, J=5, 7 Hz, 3H, $H_{5'}$), 7.19 (d, J=7 Hz, 3H, $H_{3'}$), 7.48 (t, J=7 Hz, 3H, $H_{4'}$), 8.48 (d, J=5 Hz, 3H, $H_{6'}$). HR ES-MS (CH_3CN/HCOOH): 490.1451. Required for $[C_{27}H_{27}N_3S_3{\cdot}H]^+$ 490.1445. Analysis. $C_{27}H_{27}N_3S_3$ requires: C, 66.22; H, 5.56; N, 8.58. Found: C, 66.17; H, 5.57; N, 8.48.

X-Ray structural analysis of **1**: formula $C_{27}H_{27}N_3S_3$, M=489.70, colourless crystal 0.75×0.70×0.05 mm^3, a=16.335(6), b=10.087(4), c=16.939(6) Å, β=118.223(4)°, V=2459.1(15), ρ_{calcd}=1.323 g cm^{-1}, Z=4, monoclinic, $P2_1/n$, T=168(2) K, $2\theta_{max}$=53.0°, 30408 reflections collected, 5034 unique, 3006 observed, $R1$=0.0440, $wR2$=0.1067.

3.1.2. 1,3,5-Tris(4-pyridylsulfanylmethyl)-2,4,6-trimethylbenzene (2). Reaction of 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene and 4-mercaptopyridine gave the product, which was recrystallised from hot acetonitrile as white needles. Yield: 72%. Mp: 229–231 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 2.48 (s, 9H, CH_3), 4.25 (s, 6H, CH_2), 7.17 (d, J=5 Hz, 6H, $H_{3'}$, $H_{5'}$), 8.44 (d, J=5 Hz, 6H, $H_{2'}$, $H_{6'}$). HR EI-MS: 489.13672. Required for $C_{27}H_{27}N_3S_3$ 489.13671. Analysis. $C_{27}H_{27}N_3S_3{\cdot}1/2H_2O$ requires: C, 65.09; H, 5.66; N, 8.42. Found: C, 65.44; H, 5.59; N, 8.55.

3.1.3. 1,2,4,5-Tetrakis(2-pyridylsulfanylmethyl)benzene (3).[13] X-Ray structural analysis of **3**: formula $C_{30}H_{26}N_4S_4$, M=570.70, colourless crystal 0.60×0.26×0.05 mm^3, a=8.349(4), b=8.748(4), c=11.136(6) Å, α=86.575(8), β=68.313(5), γ=63.466(6)°, V=670.7(5), ρ_{calcd}=1.413 g cm^{-1}, Z=1, triclinic, P-1, T=168(2) K, $2\theta_{max}$=53.0°, 8586 reflections collected, 2683 unique, 2077 observed, $R1$=0.0362, $wR2$=0.0852.

3.1.4. 1,2,4,5-Tetrakis(4-pyridylsulfanylmethyl)benzene (4). Reaction of 1,2,4,5-tetrakis(bromomethyl)benzene and 4-mercaptopyridine gave the product, which was recrystallized by diffusing diethyl ether into a chloroform solution. Yield: 50%. Mp: 192–193 °C. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 4.45 (s, 8H, CH_2), 7.26 (d, J=5 Hz, 8H, $H_{3'}$, $H_{5'}$), 7.56 (s, 2H, H_3, H_6), 8.32 (d, br, 8H, $H_{2'}$, $H_{6'}$). HR ES-MS (CH_3CN/HCOOH): 571.1118. Required for $[C_{30}H_{26}N_4S_4{\cdot}H]^+$ 571.1119. Analysis: $C_{30}H_{26}N_4S_4{\cdot}1/4CHCl_3$ requires: C, 60.48; H, 4.41; N, 9.32. Found: C, 60.20, H, 4.29; N, 9.18.

3.1.5. 1,2,3,4-Tetrakis(2-pyridylsulfanylmethyl)benzene (5). Reaction of 1,2,3,4-tetrakis(bromomethyl)benzene and 2-mercaptopyridine gave the product, which was recrystallized from acetone/ethanol solution at 0 °C. Yield: 50%. Mp: 80–81 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 4.56 (s, 4H, $CH_{2\ out}$), 4.76 (s, 4H, $CH_{2\ in}$), 6.89 (dd, J=7, 5 Hz, 2H, $H_{5'\ in}$), 6.93 (dd, J=7, 5 Hz, 2H, $H_{5'\ out}$), 7.12 (m, 4H, $H_{3'\ in,out}$), 7.33 (s, 2H, H_5, H_6), 7.42 (m, 4H, $H_{4'\ in,out}$), 8.21 (d, J=5 Hz, $H_{6'\ in}$), 8.35 (d, J=5 Hz, 2H, $H_{6'\ out}$). HR ES-MS (CH_3CN/HCOOH): 571.1117. Required for $[C_{30}H_{26}N_4S_4{\cdot}H]^+$ 571.1119. Analysis. $C_{30}H_{26}N_4S_4$ requires: C, 63.12; H, 4.59; N, 9.81. Found: C, 62.84; H, 4.80; N, 9.69.

3.1.6. Hexakis(2-pyridylsulfanylmethyl)benzene (6). Reaction of hexakis(bromomethyl)benzene and 2-mercaptopyridine gave the product, which was recrystallized from dimethylformamide solution as a white microcrystalline solid. Yield: 81%. Mp: 224–226 °C. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 4.62 (s, 12H, CH_2), 7.02 (dd, J=7.5, 5 Hz, 6H, $H_{5'}$), 7.27 (d, J=7.5 Hz, 6H, $H_{3'}$), 7.59 (t, J=7.5 Hz, 6H, $H_{4'}$), 8.05 (d, J=5 Hz, 6H, $H_{6'}$). ES-MS (CH_3CN/HCOOH): 817.2 $[M{\cdot}H]^+$, 409.1 $[M{\cdot}2H]^{2+}$. Analysis. $C_{42}H_{36}N_6S_6$ requires: C, 61.72; H, 4.44; N, 10.28. Found: C, 61.48; H, 4.42; N, 10.34.

3.1.7. Hexakis(4-pyridylsulfanylmethyl)benzene (7). Reaction of hexakis(bromomethyl)benzene and 4-mercaptopyridine gave the product which was recrystallized by diffusion of petroleum ether (50–70) into a pyridine solution as colourless plates. Yield: 90%. Mp: 205–207 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 4.39 (s, 12H, CH_2), 7.05 (d, J=5 Hz, 12H, $H_{3'}$, $H_{5'}$), 8.36 (d, J=5 Hz, 12H, $H_{2'}$, $H_{6'}$). HR ES-MS (CH_3CN/HCOOH): 817.1409. Required for $[C_{42}H_{36}N_6S_6{\cdot}H]^+$ 817.1404. Analysis. $C_{42}H_{36}N_6S_6$ requires: C, 61.72; H, 4.44; N, 10.28. Found: C, 61.78; H, 4.79; N, 10.61.

X-Ray structural analysis of **7**: formula $C_{44}H_{41}N_6S_6O_{0.5}$, M=854.19, colourless crystal 0.25×0.25×0.15 mm^3, a=13.117(7), b=20.574(12), c=8.862(5) Å, β=106.007(19)°, V=2299(2), ρ_{calcd}=1.234 g cm^{-1}, Z=2, monoclinic, $P2_1/c$, T=168(2) K, $2\theta_{max}$=53.0°, 21965 reflections collected, 4676 unique, 2484 observed, $R1$=0.0466, $wR2$=0.1230.

3.1.8. Octakis(2-pyridylsulfanylmethyl)biphenylene (8). Octamethylbiphenylene (50 mg, 0.19 mmol) and *N*-bromosuccinimide (541 mg, 3.04 mmol) were brought to reflux in CCl_4 (15 mL). Dibenzoyl peroxide (5 mg) was added and the solution irradiated for 2.5 hours to give a bright yellow suspension. This was cooled and the solvent removed. The yellow residue was suspended in acetone and filtered, washed with acetone and diethyl ether and dried. Yield: 74 mg (43%). ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 4.71 (s, 8H, $CH_{2\ in/out}$), 4.78 (s, 8H, $CH_{2\ in/out}$)). EI-MS m/z 895 $[M]^+$, 814 $[M-Br]^+$, 737 $[M-2Br]^+$, 657 $[M-3Br]^+$, 579 $[M-4Br]^+$, 497 $[M-5Br]^+$, 419 $[M-6Br]^+$. Analysis. $C_{20}H_{16}Br_8$ requires: C, 26.82; H, 1.80. Found: C, 27.08; H, 1.89. Octakis(bromomethyl)biphenylene (100 mg, 0.11 mmol) was reacted with 2-mercaptopyridine (109 mg, 0.98 mmol), as above, to give the product as a yellow solid. Yield: 91 mg (71%). Mp: 195–197 °C. Diffusion of diethyl ether into a chloroform solution gave deep yellow needles. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 4.45 (s, 8H, $CH_{2\ in}$), 4.57 (s, 8H, $CH_{2\ out}$), 6.74 (dd, J=7.5, 5 Hz, 4H, $H_{5'\ in}$), 6.82 (dd, J=7.5, 5 Hz, 4H, $H_{5'\ out}$), 6.97 (d, J=7.5 Hz, 4H, $H_{3'\ in}$), 7.09 (d, 7.5 Hz, 4H, $H_{3'\ out}$), 7.25 (t, J=7.5 Hz, 4H, $H_{4'\ in}$), 7.37 (t, J=7.5 Hz, 4H, $H_{4'\ out}$), 7.92 (d, J=5 Hz, 4H, $H_{6'\ in}$), 8.06 (d, J=5 Hz, 4H, $H_{6'\ out}$). ES-MS (CH_3CN/HCOOH) 1137.0 $[M{\cdot}H]^+$. Analysis. $C_{60}H_{48}N_8S_8$ requires: C, 61.40; H, 4.46. Found: C, 61.46; H, 5.07.

X-Ray structural analysis of **8**: formula $C_{67}H_{65}N_8S_8O_2$, M=1270.75, colourless crystal 0.60×0.30×0.30 mm^3, a=22.217(6), b=25.718(8), c=11.618(3) Å, V=6638(3), ρ_{calcd}=1.271 g cm^{-1}, Z=4, orthorhombic, $Ccca$, T=168(2) K, $2\theta_{max}$=53.0°, 23257 reflections collected, 3385 unique, 2134 observed, $R1$=0.0416, $wR2$=0.1190.

Acknowledgements

We thank the Royal Society of New Zealand Marsden Fund for financial support and Dr Christopher M. Hartshorn for some preliminary results.

References

1. (a) Menger, F. M.; Azov, V. A. *J. Am. Chem. Soc.* **2002**, *124*, 11159–11166. (b) Gringas, M.; Pinchart, A.; Dallaire, C. *Angew. Chem. Int. Ed.* **1998**, *37*, 3149–3151.
2. Vögtle, F.; Weber, E. *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 814–816.
3. MacNicol, D. D.; Downing, G. A. *Comprehensive Supramolecular Chemistry*; Elsevier: Oxford, 1996; Vol. 6. pp 421–464, and references therein.
4. Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071–4097.
5. See, for example (a) Cammidge, A. N.; Gopee, H. *J. Mater. Chem.* **2001**, *11*, 2773–2783. (b) Boden, N.; Bushby, R. J.; Cooke, G.; Lozman, O. R.; Lu, Z. *J. Am. Chem. Soc.* **2001**, *123*, 7915–7916. (c) Tang, B. Y.; Ge, J. J.; Zhang, A.; Calhoun, B.; Chu, P.; Wang, H.; Shen, Z.; Harris, F. W.; Cheng, S. Z. D. *Chem. Mater.* **2001**, *13*, 78–86.
6. Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules: Concepts, Syntheses, Perspectives*; VCH: New York, 1996.
7. Guerrero, A. M.; Jalón, F. A.; Manzano, B. R.; Claramunt, R. M.; Santa María, M. D.; Escolástico, C.; Elguero, J.; Rodríguez, A. M.; Maestro, M. A.; Mahía, J. *Eur. J. Inorg. Chem.* **2002**, 3178–3189.
8. Hennrich, G.; Anslyn, E. V. *Chem. Eur. J.* **2002**, *8*, 2219–2224.
9. Taha, M.; Marks, V.; Gottlieb, H. E.; Biali, S. E. *J. Org. Chem.* **2000**, *65*, 8621–8628.
10. (a) Hartshorn, C. M.; Steel, P. *J. Chem. Commun.* **1997**, 541–542. (b) Hay, B. P.; Dixon, D. A.; Vargas, A.; Garza, J.; Raymond, K. N. *Inorg. Chem.* **2001**, *40*, 3922–3935. (c) Holm, R. H.; Kennepohl, P.; Solomon, E. I. *Chem. Rev.* **1996**, *96*, 2239–2314. (d) Walsdorff, C.; Saak, W.; Pohl, S. *J. Chem. Soc., Dalton Trans.* **1997**, 1857–1861.
11. (a) McMorran, D. A.; Steel, P. J. *J. Chem. Soc., Dalton Trans.* **2002**, 3321–3326. (b) McMorran, D. A.; Steel, P. J. *Supramol. Chem.* **2002**, *14*, 79–85. (c) McMorran, D. A.; Pfadenhauer, S.; Steel, P. J. *Inorg. Chem. Commun.* **2002**, *5*, 449–451. (d) Steel, P. J.; Sumby, C. J. *Chem. Commun.* **2002**, 322–323. (e) Fitchett, C. M.; Steel, P. J. *Inorg. Chim. Acta* **2000**, *310*, 127–132.
12. Note that **3**, **5** and **6** have been mentioned in Ref. 2. However, with the exception of a melting point for **6**, no experimental details, characterization or chemistry of these was reported.
13. The preparation of **3** has been reported previously by our group Hartshorn, C. M.; Steel, P. J. *J. Chem. Soc., Dalton Trans.* **1998**, 3935–3940.
14. Smith, L. I.; Moyle, C. L. *J. Am. Chem. Soc.* **1933**, *55*, 1676–1682.
15. Hart, H.; Teuerstein, A. *Synthesis* **1979**, 693–695.
16. (a) McMorran, D. A.; Steel, P. J. *Chem. Commun.* **2002**, 2120–2121. (b) McMorran, D. A., Steel, P. J., manuscript in preparation.
17. MacNicol, D. D.; Mallinson, P. R.; Robertson, C. D. *J. Chem. Soc., Chem. Commun.* **1985**, 1649–1651.
18. (a) Werz, D. B.; Gleiter, R.; Rominger, F. *J. Am. Chem. Soc.* **2002**, *124*, 10638–10639. (b) Dai, J.; Kuroda-Sowa, T.; Munakata, M.; Maekawa, M.; Suenaga, Y.; Ohno, T. *J. Chem. Soc., Dalton Trans.* **1997**, 2363–2368.
19. (a) Lu, J.; Zhang, J.; Shen, X.; Ho, D. M.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **2002**, *124*, 8035–8041. (b) Le Magueres, P.; Lindeman, S. V.; Kochi, J. K. *Organometallics* **2001**, *20*, 115–125. (c) Le Magueres, P.; Lindeman, S. V.; Kochi, J. K. *J. Chem. Soc., Perkin Trans.* **2001**, *2*, 1180–1185. (d) Hubig, S. M.; Lindeman, S. V.; Kochi, J. K. *Coord. Chem. Rev.* **2000**, *200*, 831–873. (e) Matsuura, A.; Nishinaga, T.; Komatsu, K. *J. Am. Chem. Soc.* **2000**, *122*, 10007–10016. (f) Jones, J. B.; Brown, D. S.; Hales, K. A.; Massey, A. G. *Acta Crystallogr. Sect. C* **1988**, *44*, 1757–1759. (g) Jones, J. B.; Brown, D. S.; Massey, A. G.; Slater, P. J. *J. Fluorine Chem.* **1986**, *31*, 75–88.
20. Eckert-Maksic, M.; Hodoscek, M.; Kovacek, D.; Maksic, Z. B.; Poljanec, K. *Chem. Phys. Lett.* **1990**, *171*, 49–52.
21. van der Made, A. W.; van der Made, R. H. *J. Org. Chem.* **1993**, *58*, 1262–1263.
22. Stapler, J. T.; Bornstein, J. J. *Heterocycl. Chem.* **1973**, *10*, 983–988.
23. Backer, H. J. *Rec. Trav. Chim.* **1935**, *54*, 745–749.
24. Sheldrick, G. M. *Acta Crystallogr. Sect. A* **1990**, *46*, 467–473.
25. Sheldrick, G. M. *SHELXL-97*; University of Göttingen, Germany, 1993.