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Acid-catalysed Condensation of 1,3-Benzenedithiol with Aldehydes: A Low Dilution Preparation of 1,3,10,12-Tetrathia[3.3]metacyclophanes

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Abstract: The condensation of 1,3-benzenedithiol with aliphatic aldehydes and ferrocenecarboxaldehyde under acid catalysis in ethanol gave 2,11-disubstituted-1,3,10,12-tetrathia[3.3]metacyclophanes in poor to moderate yield. Each isolated macrocycle was found to consist of two geometric isomers, the proportions of which varied with each aldehyde used. Variable temperature NMR studies confirmed the extreme flexibility of the (R = Me) system, which crystallises mainly as the cis isomer.

INTRODUCTION

In contrast to the syntheses and studies of 2,11-dithia[3.3]metacyclophanes,[1] the investigation of 1,3-benzenedithiol-derived 1,3,10,12-tetrathia[3.3]metacyclophanes **1** has received little attention. Only the preparation in 1971 of **1a-c** by Vögtle and Lichtenthaler[2] has, to our knowledge, been reported; single isomers of **1a-c** were obtained but their absolute configuration could not be ascertained. An alternative synthesis, assignment of configuration and conformational analysis of **1b** is reported herein, with the application of this preparation to the generation of a novel ferrocenyl-appended tetrathia[3.3]metacyclophane. The electrochemical properties of this and an acyclic bisferrocene model compound are discussed.

RESULTS AND DISCUSSION

The addition of concentrated hydrochloric acid to an equimolar solution of 1,3-benzenedithiol and acetaldehyde in ethanol, followed by refluxing for >25 h yielded a white precipitate, shown by spectroscopic techniques to be cyclic dimer, **1b** in 5 % yield (Figure 1).

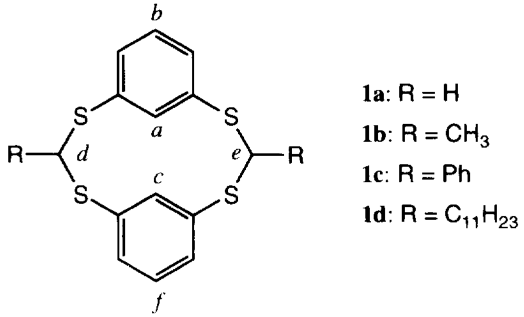


Figure 1. 2,11-Disubstituted-1,3,10,12-tetrathia[3.3]metacyclophanes **1**.

FAB Mass spectrometry gave evidence of a cyclic trimer and tetramer in samples of crude product, with ions at *m/z* 504 and *m/z* 673, respectively. The malodorous gel-like by-product formed in the preparation of **1b** in comparatively large quantities was studied by GC-MS and was found to consist of a complex mixture of starting materials and partially condensed compounds and isomers thereof.

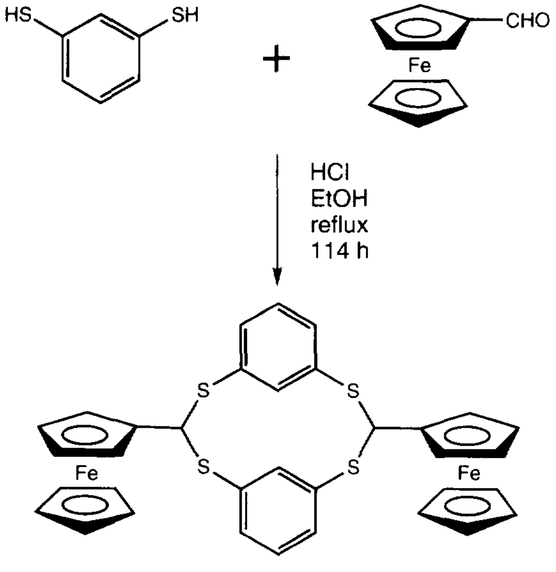
The condensation of 1,3-benzenedithiol with dodecanal, using hydrochloric acid in ethanol, generated another [3.3]metacyclophane, **1d**, in 7 % yield. However, despite size exclusion chromatographic separation and the obtention of colourless needle-like crystals, the product continued to be contaminated with an oily unknown by-product. This persistent oily impurity is thought to be a mixture of partially condensed species analogous to the by-products formed in the preparation of **1b**.

The use of ferrocenecarboxaldehyde in the condensation reaction (under identical conditions), yielded no oily by-product but a brown precipitate instead (Scheme 1). The yields of this crude brown material was 39-62 %. The extraction of this crude solid with toluene yielded a golden waxy solid, which was shown by FAB-MS to consist of a mixture of cyclo-oligomers up to and including the cyclic pentamer (ions at *m/z* 676, 1014, 1352 and 1691). The separation and isolation of each cyclic oligomer proved difficult, especially for the higher oligomers. Two column chromatographic separations of the crude extract had little effect, but a bright yellow solid was isolated by exploitation of its lower solubility in toluene. This isolated material was confirmed by FAB-MS to be the cyclic dimer, **1e**, obtained in 28% yield, which was further purified by size-exclusion chromatography using Sephadex. The aldehyde carbonyl stretches in the IR spectra of **1b** and **1e** were absent, as were the bands corresponding to the thiol S-H stretch, which occur at 2600-2550 cm^{-1}.

Another ferrocenecarboxaldehyde/dithiol condensation has recently been reported by Bartsch and co-workers,[3] where the aldehyde was reacted with a range of oligo(ethyleneoxy)- and other aliphatic dithiols under

Lewis acid catalysis (BF_3) to generate ferrocenyl thioacetal crown ethers in high yields, with the metallocene as a pendant unit.

It is noteworthy that metacyclophanes **1b**, **1d** and **1e** were generally formed, albeit in poor yields in the cases of **1b** and **1d**, in quite concentrated reaction mixtures. Dilution and acid concentration may be responsible for the difference in yield of the crude product in the 1,3-benzenedithiol/ferrocenecarboxaldehyde condensations: the first reaction used 10 mmol reactants in 10 mL ethanol with 1.5 mL acid catalyst (crude yield 39 %) whereas the second reaction used 20 mmol reactants in 40 mL ethanol with only 1.7 mL acid catalyst (crude yield 62 %). Thus optimisation of this condensation may lie towards a slightly higher dilution with a concomitant decrease in acid catalyst concentration.

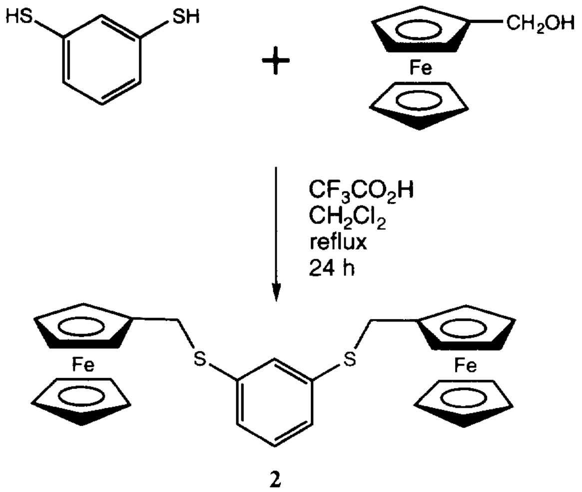


1e

Scheme 1. Acid-catalysed condensation of 1,3-benzenedithiol with ferrocenecarboxaldehyde.

As an acyclic model for the preparation of the diferrocenyl[3.3]metacyclophane, bis(thioether) **2** was synthesised. Scheme 2 outlines the reaction used in the preparation of **2** (yield 60 %); acid-catalysed attack of thiol at protonated hydroxymethylferrocene based on the procedure reported by Ratajczak,[4] which had been employed in this laboratory with success.[5]

The electrochemical properties of **1e** and **2** were studied by cyclic voltammetry in dichloromethane solutions with $NBu^n_4PF_6$ as supporting electrolyte. Compounds **1e** and **2** exhibited quasi-reversible ($E_{1/2}$ 0.60 V) and reversible ($E_{1/2}$ 0.59 V) one electron oxidation waves, respectively, the two ferrocenyl units of each compound being essentially electronically equivalent and independent.[6]



Scheme 2. Synthesis of bis(thioether) **2**.

STEREOCHEMISTRY OF THE TETRATHIA[3.3]METACYCLOPHANES

Due to the pivotal carbons *d* (C-2) and *e* (C-11), derived from the carbonyl group of the aldehyde used, the 2,11-disubstituted-1,3,10,12-tetrathia[3.3]metacyclophane structure gives rise to three possible geometric isomers. These are the (cis)ee, (trans)ea and (cis)aa isomers, considering only the *syn*-conformation of the 1,3-dithioaryl groups of the system (e = equatorial, a = axial) (Figure 2).

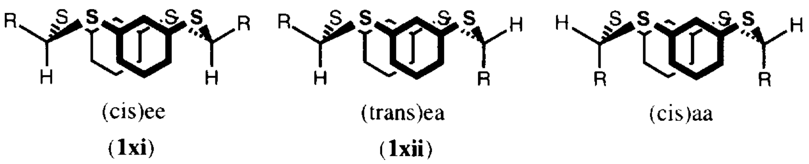


Figure 2. The three possible geometric isomers of 2,11-disubstituted-1,3,10,12-tetrathia-[3.3]metacyclophanes **1x** in the *syn*-conformation (e = equatorial, a = axial).

The Configurations of the Tetrathia[3.3]metacyclophanes

The synthesis of **1b** and the 2,11-diphenyl analogue **1c** reported by Vögtle and Lichtenthaler[2] in 1971 involved the S_N2 reaction of the disodium salt of 1,3-benzenedithiol with *gem*-dihalide compounds, 1,1-dibromoethane and (dichloromethyl)benzene respectively, under high dilution conditions in *n*-butanol. The yields of **1b** and **1c** were 12% and 30% respectively. According to this short paper, the ^{1}H NMR spectra of the cyclophanes investigated (**1b** and **1c**) did not allow any definite statements about the geometric orientation of the R-groups in the two macrocyclic systems. The ^{1}H NMR spectral data they obtained pointed to the synthesis of only one geometric isomer with cis or trans orientation with respect to carbons *d* and *e* (C-2 and C-11).

Interestingly, the synthesis of **1b** by the acid-catalysed condensation of 1,3-benzenedithiol with acetaldehyde yielded a product which, on the evidence of ^{1}H NMR spectral data, appeared to consist of *more than one isomer*. Table 1 gives the ^{1}H NMR spectral and other data for **1b** as published in reference 2 with the corresponding data obtained for **1b** formed by acid-catalysed condensation, whose isomers, for the purpose of discussion, are designated as **i** and **ii**.

Table 1. Comparison of published[2] with recorded data for cyclophane **1b** (**i** and **ii** refer to the two isomers observed in the sample prepared by the condensation reaction).

Compound	Preparative Method	m. p. (°C)		^{1}H NMR Data[a] (ppm)		
				$\delta(H_i)$[b]	δ(C-H)	$\delta(CH_3)$
1b	S_N2	183-188		7.5	5.2 q	1.7 d
1b	Condensation	150-151	**i**	7.60[c]	5.31 q	1.69 d
			ii	8.00	6.03 q	1.67 d

[a] Both samples were analysed as solutions in DMSO-d_6 (q = quartet, d = doublet).
[b] H_i = intraannular protons (H_b and H_c).
[c] 300 MHz Spectrophotometer used. Field strength of machine used in reference 2 was not quoted.

The ^{1}H NMR spectra of (impure) **1d** and **1e** also yielded two signals for the CHR methine proton derived from the aldehyde, and two signals for the intraannular protons H_i (H_a and H_c). The chemical shifts of these protons in **1d** and **1e** as well as those in **1b**, are given in Table 2. All spectra were recorded as solutions in deuteriochloroform (at 300 MHz for **1d** and **1e**, and at 400 MHz for **1b**). It is implied by the ^{1}H NMR spectral data in Table 1 that isomer **1bi** obtained in the condensation reaction is the same as the single isomer obtained by Vögtle and co-workers. Several samples of **1b** have been prepared with little modification of the recipe and they all showed signals in their respective ^{1}H NMR spectra for more than one isomer, very probably two.

Table 2. Some ^{1}H NMR chemical shifts of 1,3,10,12-tetrathia[3.3]metacyclophanes in $CDCl_3$ (ppm).

Compound	δ (H_i)	δ (CHR)	δ (R)	
1bi[a]	7.51 t	4.98 q[b]	1.79 d[b]	CH_3
1bii	7.62 t	5.02 q[b]	1.78 d[b]	CH_3
1di	7.43 t	4.69 t		
1dii	7.48 t	4.78 t		
1ei	7.59 s	5.67 s		
1eii	7.66 s	5.80 s		

[a] Suffixes **i** and **ii** correspond to isomers designated as **i** and **ii**, respectively.
[b] Signals overlap (though data analysis was unaffected; s = singlet, q = quartet, d = doublet).

A 400 MHz ^{1}H NMR spectrum of **1b** in deuteriochloroform is shown in Figure 3. The spectrum consists of two duplicate spectra, with one slightly offset from the other. The corresponding integrations and signals of each spectrum match each other exactly, demonstrating that for this sample of **1b**, a 1:1 ratio of isomers is formed. The presence of two geometrical isomers may also account for the marked difference between the recorded and published melting points (Table 1).

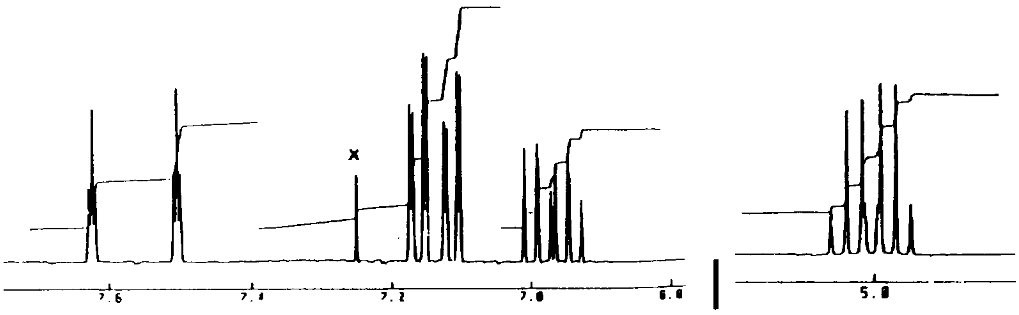


Figure 3. 400 MHz ^{1}H NMR spectrum of **1b** in $CDCl_3$ (not to scale).
Methyl signals at δ 1.8 are omitted for clarity. X = undeuterated solvent signal.

The slow evaporation of a dilute dichloromethane solution of **1b** yielded colourless crystals suitable for analysis by X-ray crystallography. The isomer distribution in this crystalline sample of **1b** was found by ^{1}H NMR spectroscopy to be approximately 4:1 isomer **i**:isomer **ii**. The structure of the crystal chosen for diffraction consists of molecules of **1bi** only (Figure 4) which contain crystallographic C_2 symmetry. Bond lengths and angles were as expected. The planes of the two phenyl rings intersect at an angle of 47.3° across the two-fold axis. There were no intramolecular contacts less than the sum of the van der Waals' radii.

The melting point of the crystalline sample was found to be 179-182 °C and comparison of this value with that of the 1:1 isomer **i**:isomer **ii** sample shown in Table 1, bearing in mind the change in isomeric distribution, is further evidence that isomer **i** and the sample prepared by Vögtle are identical.

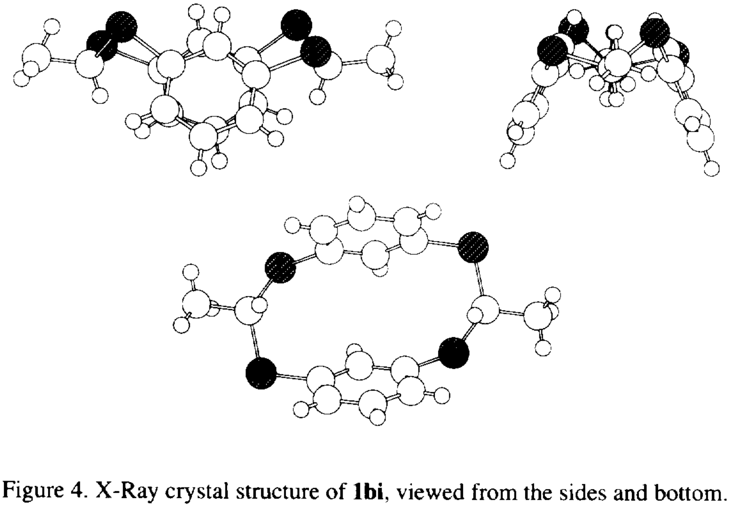


Figure 4. X-Ray crystal structure of **1bi**, viewed from the sides and bottom.

The Conformations of the Tetrathia[3.3]metacyclophanes

According to Vögtle,[2] the existence of a discrete rigid conformation was improbable, and all compounds **1a**, **1b** and **1c** had practically unlimited conformational mobility. Intraannular steric interactions were not detected. Figure 5 gives the sketched rotation processes under consideration for the intramolecular flexibility of the three cyclophanes **1a-c** in the cis configuration (with the R-substituents on carbons *d* and *e*).

Thus, from the diagram in Figure 5, it is suggested by Vögtle that the sterically least hindered and strained forms are Syn-I and Syn-VI, and due to the conformational flexibility of the macrocyclic system, the (cis)ee (Syn-I) and (cis)aa (Syn-VI) isomers are mutually interconvertible. Therefore, only one isomer with cis-configuration can exist.

A variable temperature (VT) ^1H NMR spectroscopic study was carried out on a sample of **1b** derived from the crystals. The crystals used were thoroughly crushed, and dried in an oven to remove any residual solvent of crystallisation (CH_2Cl_2). A solution of ~10 mg of **1b** in ~0.5 ml DMSO-d_6 was prepared and spectra were recorded at 20° interval increases from the ambient starting temperature (291 K). Comparatively little change in signal shape was observed in the spectra recorded at the higher temperatures with respect to the 291 K spectrum, with the signals in the 391 K spectrum just beginning to split into two. However, considerable shifts were observed in the positions of the characteristic signals (quartets) corresponding to the methine CH-R groups, along with smaller displacements of the intraannular aryl protons H_i (t) signals and methyl doublets (Table 3).

Table 3. ^1H NMR chemical shifts of **1b** with change in temperature (DMSO-d_6 solutions were used).

Isomer	$\delta(H_i)$ [$\Delta\delta$][a]	δ(CH-R) [$\Delta\delta$]	$\delta(CH_3)$ [$\Delta\delta$]	T (K)
i	7.61	5.31	1.69	291
ii	8.00	6.03	1.67	291
i	7.52 [-0.09]	5.19 [-0.12]	n/a[b]	371
ii	7.85 [-0.15]	5.72 [-0.31]	n/a	371
i	7.50 [-0.11]	5.16 [-0.15]	1.75 [+0.06]	391
ii	7.81 [-0.19]	5.64 [-0.39]	1.76 [+0.09]	391

[a] Values are in ppm.
[b] n/a = not available.

A cold VT NMR study was carried out using the same crystal-derived sample, this time using deuteriochloroform as the solvent. The broadening of the sharp methine quartet and methyl doublet signals as the temperature was decreased from 291 K to 211 K is shown in Figure 6.

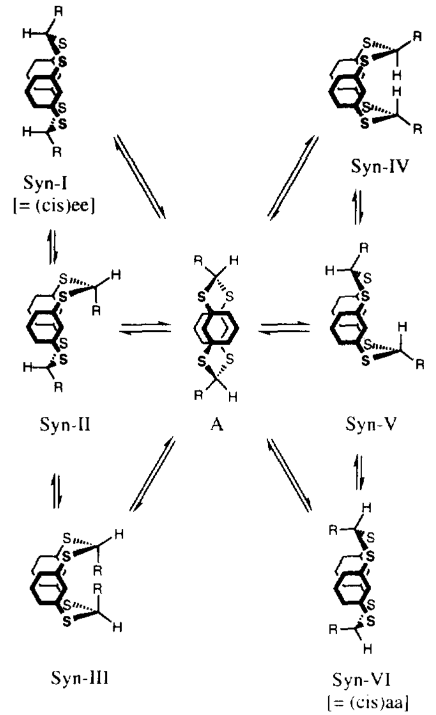


Figure 5. The conformational mobility of the [3.3]metacyclophanes.
The rotation processes for the cis configuration at carbons *d* and *e* (C-2 and C-11) are shown.
Syn = *syn* -conformation and A = *anti*-conformation with respect to the **bold** benzene ring.
Only the resulting conformations from the flipping of this benzene are shown. Reproduced from reference 2.

The dramatically simplified and broad spectrum at 211 K indicated that this temperature is approaching the coalescence temperature (T_c) of conformational mobility. The very low value of T_c of both isomers of **1b** ($T_c \leq$ 211 K) implied by this data makes any attempt at conformational freezing and its observation very difficult, and highlights the rapidity of the rotation processes of **1b** at ambient temperature as well as its limitless flexibility, which is in accordance with Vögtle's hypothesis.[2]

The observed difference in isomeric distribution in **1b** derived from its two different preparations may be explained by mechanistic considerations whereby the protonation of the aldehyde generates a planar carbocation tautomer $CH_3C^+H(OH)$, which is susceptible to attack by -SH from the front of the plane, or from behind. The direction of attack of -SH only becomes crucial to the stereochemistry of the cyclophane in the final ring closure reaction. This is in contrast to Vögtle's S_N2 synthesis where the formation of a single isomer may be attributed to the thiolate nucleophile having only one possible direction of attack at the corresponding $ArSCH(CH_3)Br$ intermediate used due to the latter's tetrahedral centre. The disparity in isomeric distribution in the synthesis of **1d** and **1e** is more difficult to rationalise, the steric bulk of the aldehyde R-group and the fewer degrees of freedom possibly playing a role.

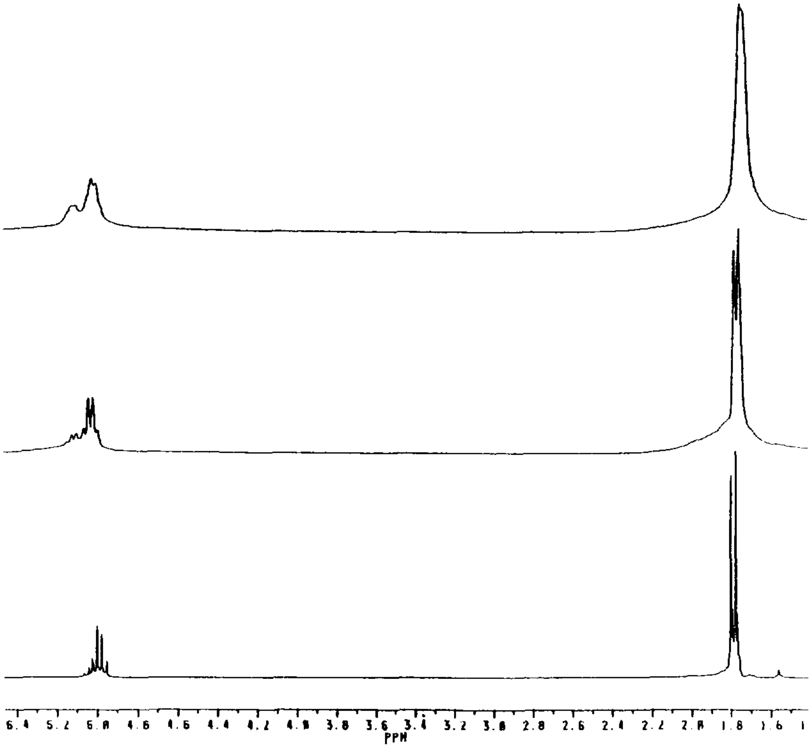


Figure 6. Methyl and methine regions of the 300 MHz ^{1}H NMR spectra of **1b** in $CDCl_3$ at 211 K (top), 231 K (middle) and 291 K (bottom).

CONCLUSIONS

The condensations of 1,3-benzenedithiol with aldehydes under acid catalysis in ethanol were found to yield 2,11-disubstituted-1,3,10,12-tetrathia[3.3]metacyclophanes **1b**, **1d**, and **1e** as isolable products in poor (R = alkyl) to moderate (R = ferrocenyl) yields. An acyclic analogue of **1e** was also prepared.

The isolated metacyclophane dimers formed consisted of two configurational isomers - (cis)ee (isomer **i**) and (trans)ea (isomer **ii**), and the isomeric distribution of each sample of **1b** prepared using acetaldehyde in repeat reactions was found to be constant at 1:1 (cis)ee:(trans)ea. Slow crystallisation enriched the (cis)ee isomer to approximately 4:1 (cis)ee:(trans)ea, each isomer crystallising separately. The isomeric distribution varied for each aldehyde used. The extreme conformational mobility of the dimethyl cyclophane **1b** was confirmed by VT ^{1}H NMR spectroscopic studies, and implies that the (cis)ee and (cis)aa isomers are mutually interconvertible and therefore constitute a single configurational isomer (isomer **i**), which is in keeping with Vögtle's proposal.[2] The prediction by Vögtle that the *syn*-conformation of the single (cis) isomer of **1b**, with the pivotal carbons *d* and *e* also positioned below the S_4 plane in a *syn* arrangement, would be the most stable conformer was confirmed by X-ray crystallographic analysis of **1bi**.

Acknowledgement: We thank the SERC for a CASE studentship to S.M.L. and for the use of the mass spectrometry and NMR services at University College, Swansea and the University of Warwick, respectively.

EXPERIMENTAL SECTION

General: All elemental analyses were carried out by the microanalytical services at either the University of Birmingham or the Inorganic Chemistry Laboratory, University of Oxford. NMR spectra were recorded on a Brücker AM 300 instrument unless otherwise stated, operating at 300 MHz for ^{1}H NMR and 75.42 MHz for ^{13}C NMR spectra. Other NMR spectra were recorded on a Brücker WH 400 instrument at the University of Warwick by the SERC NMR Spectroscopy Service. Infrared spectra were recorded on a Mattson 10410E "polaris" Fourier Transform Spectrometer as KBr discs. Electrochemical measurements were conducted on a Princeton Applied Research Potentiostat/Galvanostat Model 273. Fast atom bombardment (FAB) mass spectra were carried out at University College, Swansea by the SERC Mass Spectrometry Service and melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. The GC-MS analysis was carried out by the Analytical Services department at Zeneca Specialties. Commercial grade chemicals were used without further purification. Hydroxymethylferrocene was prepared by refluxing ferrocenomethyltrimethylammonium iodide with strong aqueous sodium hydroxide solution, followed by extraction of the reaction mixture with ether and recrystallisation from hexane.[7]

2,11-Dimethyl-1,3,10,12-tetrathia[3.3]metacyclophane, **1b**.

To a stirred solution of 1,3-benzenedithiol (5.00 g, 35.2 mmol) and acetaldehyde (1.55 g [1.97 mL], 35.2 mmol) in 35 mL absolute ethanol was added concentrated hydrochloric acid (3.52 mL), dropwise. The mixture was refluxed for 94 h under nitrogen, by which time a whitish opaque gel had precipitated. While still warm, the reaction solution above the gel (and any white solid precipitate present) was pipetted from the reaction flask and chilled in the freezer to yield a white precipitate (if not already formed). To the white ethanolic suspension was added an excess (~100 mL) 4 M aq. NaOH solution with trituration, and the mixture was filtered (sinter). The whitish residue was washed with a copious amount of water and was then taken up in 30 mL dichloromethane, dried ($MgSO_4$) and filtered. The evaporated filtrate was purified by size-exclusion chromatography (Sephadex LH 120, acetonitrile as eluent), giving a white solid as an inseparable mixture of (cis)ee and (trans)ea isomers, 0.295 g, (5%). m.p. 150-151 °C but see text; IR -CHO and -SH stretches were absent; FAB-MS *m/z* 336 M^{+} (calc. 336.6); ^{1}H NMR (400 MHz, $CDCl_3$) 1:1 isomeric ratio - (cis)ee isomer **1bi** δ: 1.9 (6H, d ^{3}J =7.2 Hz, CH_3), 4.98 (2H, q ^{3}J =7.2 Hz, CHR), 6.95 (2H, t ^{3}J =7.7 Hz, $H_{b,f}$), 7.11 (4H, dd ^{3}J =7.7 Hz,^{4}J =1.8 Hz, H_g), 7.51 (2H, t ^{4}J =1.8 Hz, $H_{a,c}$); (trans)ea isomer **1bii** δ: 1.78 (6H, d ^{3}J =7.3 Hz, CH_3), 5.02 (2H, q ^{3}J =7.3 Hz, CHR), 6.99 (2H, t ^{3}J =7.7 Hz, $H_{b,f}$), 7.16 (4H, dd ^{3}J =7.7 Hz,^{4}J =1.8 Hz, H_g), 7.62 (2H, t ^{4}J =1.8 Hz, $H_{a,c}$); ^{13}C NMR (100 MHz, $CDCl_3$) (cis)ee isomer **1bi** δ: 22.50 (CH_3), 54.44 ($\underline{C}HCH_3$), 129.13, 132.63 (Aryl-C), 134.27 (ipso-C), 138.62 (Ar-C); (trans)ea isomer **1bii** δ: 22.35 (CH_3), 55.99 ($\underline{C}HCH_3$), 129.13, 133.02 (Ar-C), 134.17 (ipso-C), 139.29 (Ar-C); Anal. (UoB) calculated for $C_{16}H_{16}S_4$ C: 57.1% H: 4.8%; Found C: 56.9% H: 4.9%.

2,11-Diundecyl-1,3,10,12-tetrathia[3.3]metacyclophane, **1d**.

The procedure for the preparation of **1d** followed that described for **1b** in 40 mmol quantities, using dodecanal, except that the reflux time was increased from 94 h to 140 h. The emulsifying properties observed of the crude material thwarted to some degree the removal of the thiolic oily by-product which contaminated the product. The warm reaction mixture was filtered through glass wool and the filtrate allowed to cool, yielding a white precipitate which was collected by filtration with washing with cold ethanol. Size-exclusion chromatography of the solid residue obtained (Sephadex LH 120, dichloromethane as eluent), gave colourless needle-like crystals contaminated with oily material, 0.92 g (7%). FAB-MS *m/z* 616 M^+ (calc. 617.1); ^1H NMR (300 MHz, $CDCl_3$) ~3:2 (cis)ee: (trans)ea isomeric ratio δ: 0.88, 1.28, 1.57-2.07 (92H, 3 x m, aliphatic H), 6.98-7.06 (4H, m, $H_{b,f}$), 7.15-7.20 (8H, m, H_g); (cis)ee isomer **1di**: 4.69 (2H, t, ^3J =6.8 Hz, CHR), 7.43 (2H, t, ^4J =1.5 Hz, $H_{a,c}$); (trans)ea isomer **1dii**: 4,78 (2H, t, ^3J =6.7 Hz, CHR), 7.48 (2H, t, ^4J =1.6 Hz, $H_{a,c}$).

2,11-Ferrocenyl-1,3,10,12-tetrathia[3.3]metacyclophane, **1e**.

To a stirred solution of 1,3-benzenedithiol (2.84 g, 20 mmol) and ferrocene-carboxaldehyde (4.28 g, 20 mmol) in 40 mL absolute ethanol was added concentrated hydrochloric acid (1.70 mL, 20 mmol), dropwise. A reddish-brown gummy solid formed immediately. The mixture was refluxed for 114 h (initially, the gummy material is converted to lumps of brittle solid which are coarsely crushed to maintain the stirring). The cooled reaction mixture was evaporated to dryness and the dark solid residue was extracted with 20 x 50 mL toluene (the extraction consisting of shaking the residue with an aliquot of solvent and then decanting the coloured solution). The extracts were combined, dried ($MgSO_4$) and then filtered through Celite. The resulting filtrate was evaporated to yield a mixture of yellow solid and orange oily material. This crude material was treated with 30 mL toluene with careful swirling to give a slurry of yellow solid in a deep red-brown solution. This slurry was filtered (sinter) and the residue washed carefully with ~10 mL cold toluene and dried in the sinter and under vacuum to yield a pale yellow solid, 1.89 g, (28%). A slightly purer sample for analysis was obtained by size-exclusion chromatography (Sephadex LH 120, dichloromethane as eluent). m.p. 204 °C (dec.); IR -CHO and -SH stretches were absent; FAB-MS *m/z* 676 M^+ (calc. 676.5); ^1H NMR (300 MHz, $CDCl_3$) ~3:1 **i**:**ii** isomeric ratio, the differing order of chemical shifts of **1ei** and **1eii** with respect to those of **1bi** and **1bii** respectively allows only a very tentative assignment of **1ei** as the (cis)ee isomer δ: 4.29 (8H, m, Fc-H), 4.36 (20H, m, Fc-H), 4.55 (8H, m, Fc-H); **1ei**: 5.60 (2H, s, CHR), 7.07 (2H, t, ^3J =7.8 Hz, $H_{b,f}$), 7.25 (4H, dd, ^3J =7.7 Hz, H_g), 7.59 (2H, t, ^4J =1.7 Hz, $H_{a,c}$); **1eii**: 5.77 (2H, s, CHR), 7.08 (2H, t, ^3J =7.3 Hz, $H_{b,f}$), 7.27 (4H, dd, ^3J =7.78 Hz, H_g), 7.65 (2H, t , ^4J =1.7 Hz, $H_{a,c}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 60.76, 64.55 (CH isomers **i** and **ii**), 67.92, 68.09, 68.58, 69.57 (Fc-C), 86.8, 87.0 (ipso Fc-C), 129.36, 129.52, 132.47, 133.63, 135.19, 138.5, 140.49 (Ar-C); Anal. calculated for $C_{34}H_{28}Fe_2S_4$ C: 60.36% H: 4.17%; Found C: 60.78% H: 4.26%.

1,3-Bis(ferrocenomethylthio)benzene, **2**.

(Hydroxymethyl)ferrocene (0.39 g, 1.8 mmol) was dissolved in 50 mL dry dichloromethane. To this was added a solution of 1,3-benzenedithiol (0.14 g, 0.99 mmol) in 20 mL dry dichloromethane and 3 drops of trifluoroacetic acid. The mixture was refluxed under nitrogen for 24 h, by which time the reaction was complete (TLC). The cooled mixture was washed with 3 x 50 mL 1 M aq. NaOH solution, followed by water, and dried ($MgSO_4$) with filtration. The solvent was evaporated and the residue separated by column chromatography (alumina, CH_2Cl_2 as eluent), to yield a golden coloured solid, 0.32 g, (60%). m.p. 170-172 °C; IR 1565 cm^{-1} aromatic C=C stretching, 2922 cm^{-1} saturated C-H stretch; EI-MS *m /z* 538 M^+ (calc. 538.3); ^1H NMR (300 MHz, $CDCl_3$) δ: 3.90 (4H, s, CH_2), 4.12, 4.15 (18H, t ^3J =1.8 Hz, m, Fc-H), 7.15 (4H, m, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 68.01 (CH_2), 68.72, 68.78 (Fc-C), 84.5 (ipso Fc-C), 127.53, 128.99, 129.35, 130.65 (Ar-C). Anal. (UoB) calculated for $C_{28}H_{26}Fe_2S_2$ C: 62.47% H: 4.87%; Found C: 63.5% H: 4.9%.

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