Synthesis, conformation and tropicity of dimethano-bridged tetradehydrothia[21]-, -[23]- and -[25]annulenes

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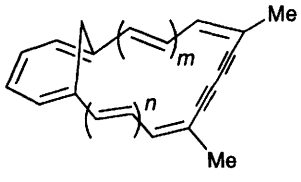
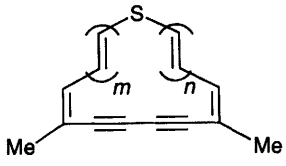
The title thiaanulenes have been synthesized through a double Wittig reaction of bis[(triphenylphosphonio)-methyl]sulfide dibromide with 6-ethynylcyclohepta-1,3,5-triene-1-carbaldehyde and/or its vinylogous aldehyde, followed by intramolecular oxidative coupling of the resulting bisethynyl sulfides. For each compound, two isomers have been isolated which differed in the geometry of their peripheral olefinic moieties. ^{1}H NMR spectra revealed that some of the geometrical isomers consisted of two conformational isomers which differed in the relative disposition of the two methano bridges. One isomer for each of the dimethano-bridged thia[21]- and -[23]annulenes sustained ring current, while the other isomers as well as those for the thia[25]annulene did not.

Introduction

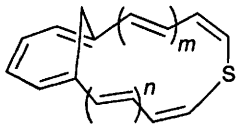
Although diatropicity or paratropicity in monocyclic conjugated systems decreases with increasing ring size,[1] a monocyclic 30-membered annulene, tetradehydro[30]annulene, has been reported to show diatropicity.[2] However, since we found that a series of methano-bridged tetradehydroannulenes **1** show diatropism up to the 34-membered ring (**1**; $m = n = 5$) in the $[4n + 2]\pi$-electron series, the presence of a bridging methylene group and a 1,3-diacetylenic linkage helps to keep the annulene perimeter rigid and planar.[3]



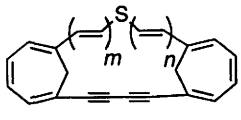
1 $m = 1$–5, $n = 1$–5



2 $m = 1$–4, $n = 1$–4



3 $m = 1$–5, $n = 1$–6



[21]-**4** $m = n = 1$

[23]-**5** $m = 1, n = 2$

[25]-**6** $m = n = 2$

The degree of dia- or para-tropicity of heteroannulenes has been found to be much smaller than that of the corresponding carbocyclic annulenes,[4] as typically shown by the fact that benzene, the parent compound of annulenes, is more diatropic than the heteroaromatics such as pyridine, pyrrole, furan and thiophene.

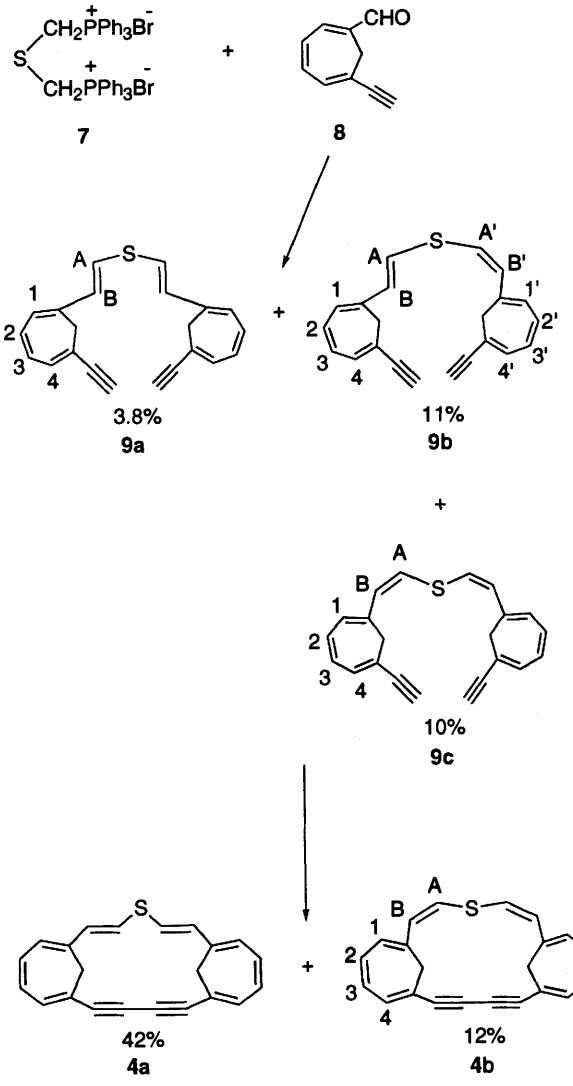
The alternation of the tropic nature between $[4n + 2]\pi$- and $[4n]\pi$-electron systems in the tetradehydrothiaannulenes **2**, due to the contribution of the lone pair electrons of the sulfur atom, has been confirmed in compounds with 13- (**2**; $m = n = 1$) to 25-membered rings (**2**; $m = n = 4$).[5–8] On the other hand in the bicyclic thiaannulenes **3** which carry one methano bridge the largest ring to show the ring current effect was found to be the 27-membered one.[9]

Since a cyclohepta-1,3,5-triene ring, which has three conjugated double bonds, together with a 1,3-diacetylene linkage has been found to contribute to maintaining annulene perimeter planarity, we considered that the dimethano-bridged thiaannulenes, formally derived from compounds **2** by replacement of two double bonds by cycloheptatriene rings, would form large π-electron systems. Thus, a thiaannulene with a larger ring size (>27-membered) showing tropicity would be obtained. With these expectations in mind, we tested whether the dimethano-bridged thiaannulenes, the title compounds, would show a similar degree of tropicity to those of the monocyclic tetradehydrothiaanulenes with the same number of the π-electrons, *e.g.* the dimethano-bridged tetradehydrothia[21]annulene **4** *vs.* dimethyltetradehydrothia[21]annulene (**2**; $m = n = 3$).

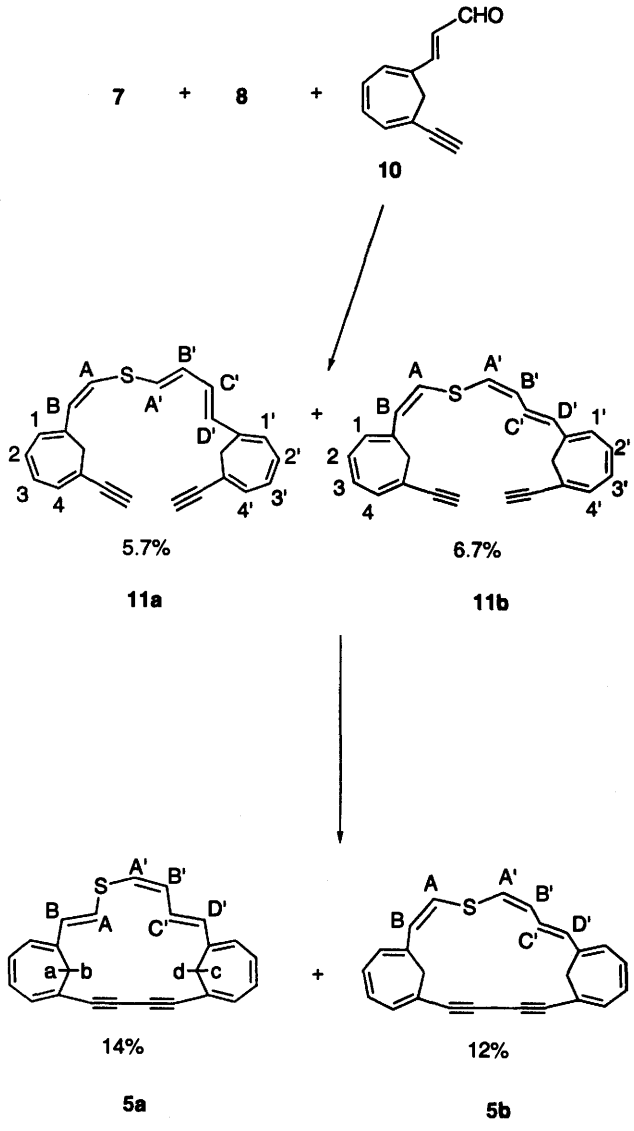
Results and discussion

Synthesis

Sondheimer and co-workers synthesized the dimethyltetradehydrothia[13]- (**2**; $m = n = 1$),[5] -thia[15]- (**2**; $m = 1$, $n = 2$)[6] and -thia[17]annulene (**2**; $m = n = 2$)[7] as well as their bis(cyclohexene)-annelated analogues[10] in which the sulfur atom is flanked on both sides by ethylenic bonds. They employed a double Wittig condensation of bis[(triphenylphosphonio)methyl]sulfide dibromide **7**[11] with an appropriate aldehyde containing a terminal acetylene group, followed by an intramolecular oxidative coupling of the resulting acyclic sulfide. We have now applied this method with advantage to the synthesis of dimethano-bridged tetradehydrothiaannulenes **4**–**6** by using 6-ethynylcyclohepta-1,3,5-triene-1-carbaldehyde **8**[12]



Scheme 1



Scheme 2

and/or its vinylogous aldehyde **10**[12] as the starting material and by essentially the same approach as that of Sondheimer and coworkers.[5–7,10]

The double Wittig reaction of 2 molar equiv. of the aldehyde **8**[12] and 1 molar equiv. of the salt **7**[11] in *N,N*-dimethylformamide (DMF) with ethanolic lithium ethoxide at 50 °C yielded a stereoisomeric mixture of the diethynyl substituted sulfide **9** in a good yield, from which three isomers, 'di-*trans*' **9a**, 'mono-*cis*' **9b** and 'di-*cis*' isomer **9c** were isolated (Scheme 1). The configuration of each isomer was confirmed by IR and ^{1}H NMR spectroscopy. Intramolecular oxidative coupling of **9** as an isomer mixture was carried out with anhydrous copper(II) acetate in pyridine and diethyl ether at 50 °C.[13] Column chromatography of the product on alumina gave the expected thia[21]annulene as two crystalline isomers **4a** and **4b** in 42 and 12% yield, respectively; they proved to be 'di-*trans*' and 'di-*cis*' isomers as discussed below.

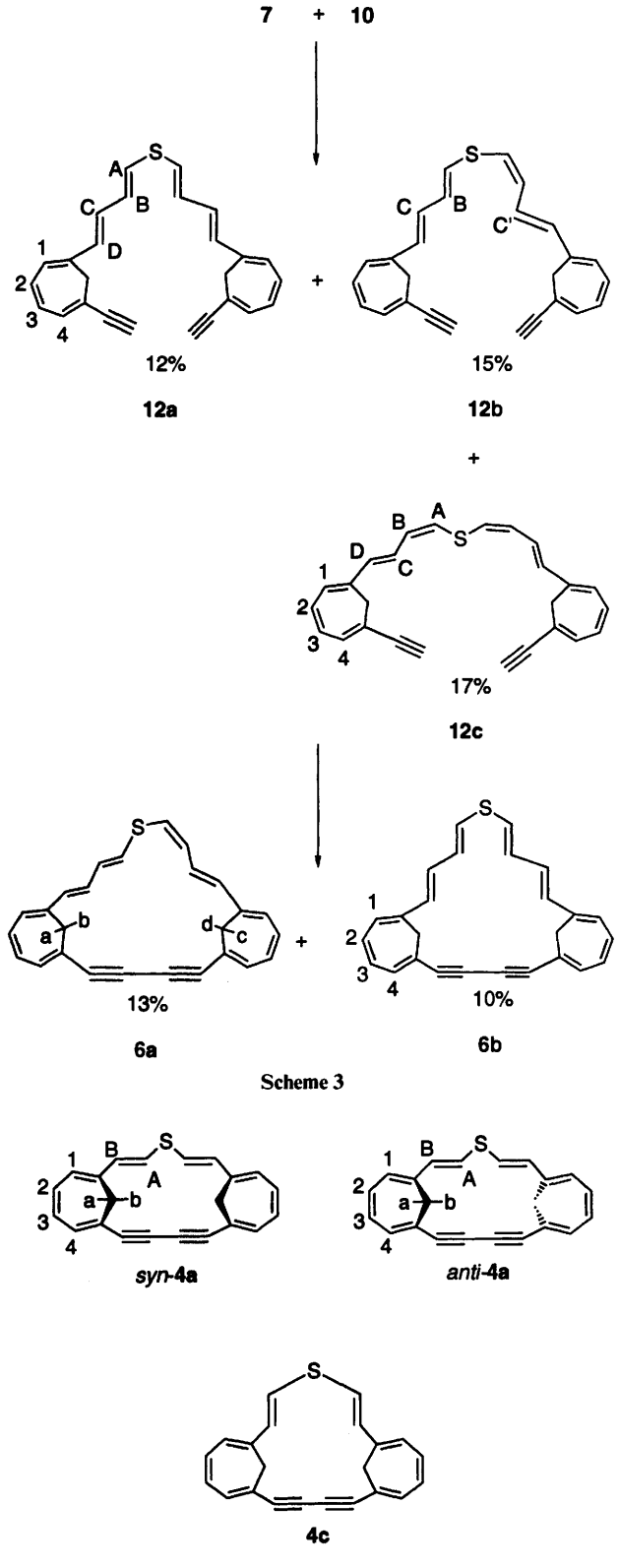
The Wittig reaction of the salt **7** with a mixture of the aldehyde **8** and the homologated aldehyde **10** yielded the unsymmetrical bisethynyl sulfide **11** as a stereoisomeric mixture, from which the 'mono-*cis*' isomer **11a** and the 'di-*cis*' isomer **11b** were isolated (Scheme 2), along with a small amount of the acyclic sulfides **9** and **12**. Oxidative coupling of **11** as the isomeric mixture afforded the thia[23]annulene; the 'mono-*cis*' **5a** and the 'di-*cis*' isomer **5b** were isolated in 14 and 12% yield, respectively (Scheme 2).

Similarly, the reaction of the salt **7** with the aldehyde **10** gave the bisethynyl sulfide **12** in a good yield as a stereoisomeric mixture, from which three isomers, 'di-*trans*' **12a**, 'mono-*cis*' **12b** and 'di-*cis*' **12c**, were isolated, only **12a** being crystalline (Scheme 3). Ring closure of the mixture **12a–c** as before gave the thia[25]annulene; the 'mono-*cis*' isomer **6a** and the 'di-*trans*' isomer **6b** were isolated in 13 and 10% yield, respectively (Scheme 3).

^{1}H NMR spectra and conformation of compounds 4–6

The major geometrical isomer **4a** of compound **4** obtained in 42% yield is shown by its ^{1}H NMR spectrum to be an equilibrium mixture of two conformational isomers in a ratio ~3:1. The conformational interconversion is slow on the NMR time scale at 24 °C [Fig. 1(*a*)] because the methylene proton signals appear as two pairs of sharp doublets at this temperature. The olefinic proton signals reveal that both of these conformers are symmetric (C_s or C_2) and the double bonds in the CH=CH–S–CH=CH moiety are of (*E*)-configuration (J_{vic} = 15.4 and 15.0 Hz). This indicates that these conformers differ in the disposition of the two methano bridges relative to the average plane of the macrocycle, *i.e. syn* and *anti*. As for the peripheral geometry, two conformations **4a** and **4c** are possible. The following facts obtained for the major conformer clearly show that **4a** is more reasonable than **4c** and the chemical shift assignments given in the Experimental section are conclusive.

(1) CH-COSY experiments reveal that the (*E*)-double bond protons at δ_H 5.924 and 6.714 are connected to the carbons at δ_C 130.24 and 128.64, respectively.



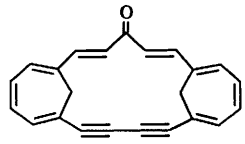
Scheme 3

4c

(2) The ^{13}C spectrum with selective ^{1}H decoupling reveals that the methylene proton at δ_H 1.222 couples with the carbon at δ_C 128.64 but not with the one at δ_C 130.24.

(3) NOE experiments reveal that the methylene proton at δ_H 2.968 is close to the proton at δ_H 5.924.

Irradiation of either one of the methylene protons of the minor conformer at 33 °C causes a decrease in the intensity of both the methylene proton signals of the major conformer due to saturation transfer. This fact indicates that the two conformers are actually *syn-anti* conformers and that the flipping takes place at a rate of the order of 10^{-1} to 10^{0} s^{-1} at this temperature, although no quantitative data are available.



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As described below in detail, compound **4a** exists as the *anti*-conformer in the crystalline state. When crystals of **4a** were dissolved in $CDCl_3$ at ~−65 °C and the solution was immediately subjected to NMR measurement at −60 °C, the spectrum revealed the presence of two conformers in a ratio ~2:1 [Fig. 1(*b*)], the major isomer being the minor one at equilibrium. The isomer ratio gradually changed and finally reached the equilibrium ratio. This fact clearly shows that the conformation of **4a** in the crystalline state corresponds to the minor conformer in solution. Therefore, the *syn* arrangement of the methano bridges was unambiguously assigned to the major conformer in solution. This is consistent with the finding that the bismethano[21]annulenone **13** prefers the *syn* conformer over *anti* in solution.[12,14]

The minor geometrical isomer **4b** obtained in 12% yield is shown to be the di-*cis* isomer (J_{vic} = 11.2 Hz). The methylene proton signals appear as a broad singlet at 24 °C, indicating the rapid occurrence of flipping of the methano bridges (Fig. 2). At −76 °C where the flipping is almost frozen on the NMR time scale, the presence of two conformers in a ratio 5:3 is observed.

Although compound **4b** was shown to exist as the *syn* conformer in the crystalline state as described below, no experiments could be made that would definitely reveal the identities of the conformers in solution, the isomerization being too fast on the laboratory time-scale even at the lowest attainable temperature of ~−100 °C.

In one isomer of **5**, obtained in 14% yield and designated **5a**, the methylene proton signals appear as four equally intense broad doublets at 24 °C, which become sharp below ~−10 °C revealing the presence of a single conformer (Fig. 3). The *syn* arrangement of the methano bridges is tentatively assumed. The signal broadening at higher temperatures reflects the interconversion between a *syn* conformer and its enantiomer by the flipping of both methano bridges. The detailed analysis of the olefinic proton region reveals that this is a 'mono-*cis*' isomer, where one of the double bonds in the –S–CH=CH–CH=CH moiety, most probably the $CH^{A'}=CH^{B'}$ bond, is of *Z*-configuration.

The other geometrical isomer **5b** isolated in 12% yield is revealed to be the 'di-*cis*' isomer where both of the S–CH=CH– bonds are *Z*. The methylene proton signals appear as much broadened peaks at room temperature (Fig. 4), which decoalesce upon lowering of the temperature and appear as two sets of four doublets with an intensity ratio ~2:1 at −89 °C, indicating the presence of two conformers in this ratio.

The lineshape of the olefinic proton signals did not significantly change down to ~−10 °C and upon further lowering of the temperature the signals broadened, split and sharpened to signals which were too complex to be analysed. Irradiation of the doublet signal at δ 4.03 at 2 °C caused an NOE upon the signal at δ 7.54 ascribed to $H^{C'}$, the only olefinic proton located inside of the ring.

Tentatively assuming that the *syn* conformer is more abundant than *anti*, the spectral change with temperature would be interpreted as follows. On the basis of the NOE result mentioned above together with the decoupling and coalescence behaviour, the methylene signals can be assigned as shown in the bottom chart of Fig. 4. The letters correspond to those shown in Scheme 4. Upon a temperature increase from −89 °C to ~0 °C, the signals c′ and d′ coalesce with c and d, respectively, while the signals a′ and b′ coalesce with b and a, respect-

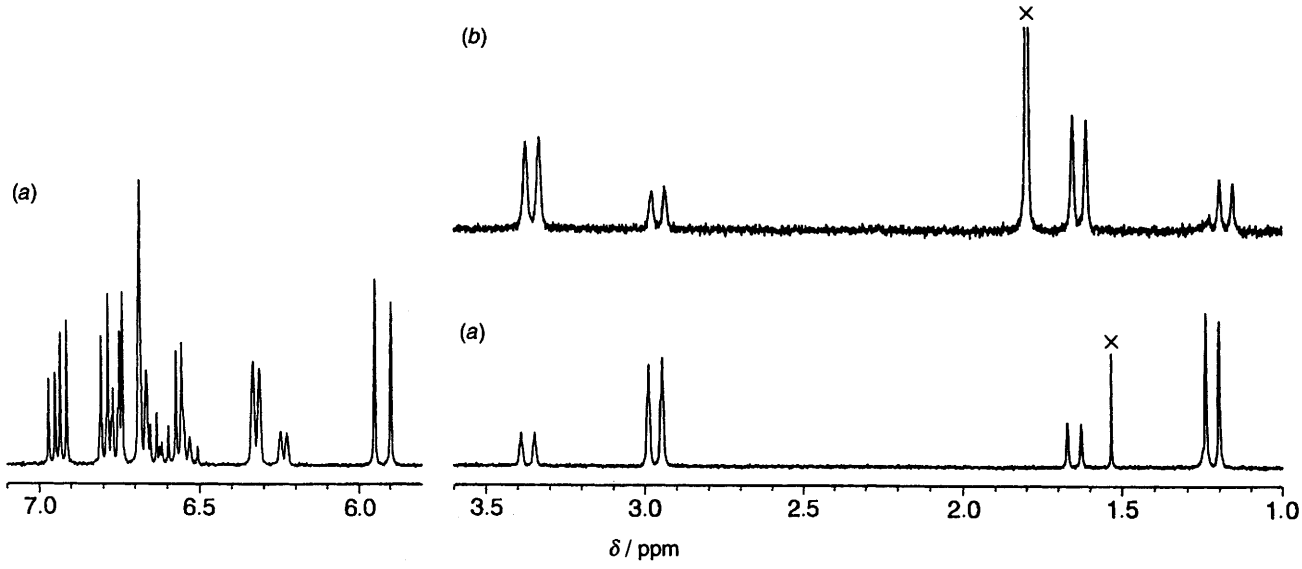


Fig. 1 ^{1}H NMR spectra of compound **4a** in $CDCl_3$ (*a*) at 24 °C in the conformationally equilibrated state, and (*b*) at ~ −60 °C immediately after dissolution of the crystalline sample of **4a** in $CDCl_3$. Peaks with × are due to water.

ively. This coalescence behaviour indicates that the flipping of the CH^aH^b bridge takes place in this temperature range, while the flipping of the CH^cH^d bridge does not. The flipping of the latter takes place above 0 °C. The interconversion barrier between A and B (and between the respective enantiomeric counterparts Ā and B̄) is roughly estimated to be ~10 kcal mol^{-1}, while that between A and B̄ (between Ā and B) ~ 15 kcal mol^{-1} (Scheme 4).

The minor isomer of compound **6** obtained in 10% yield has symmetric structure (C_s or C_2), exhibiting only 13 peaks in the ^{13}C spectrum. The methylene proton signals appear as a sharp singlet indicating rapid flipping of the methano bridges. The olefinic protons of the S–CH=CH–CH=CH moieties give rise to a non-first-order spectrum due to the small chemical-shift differences and the geometry of these moieties could not be determined. Structure **6b** with 'all-*trans*' geometry is tentatively assigned.

The major isomer of **6** obtained in 13% yield affords four equally intense doublets for the methylene protons and 26 signals in the ^{13}C spectrum at 24 °C. This indicates that the isomer exists as a single conformer with an unsymmetrical structure and that the flipping of the methano bridges is slow on the NMR time scale at 24 °C. The olefinic proton region spectrum is too complex to be fully analysed.

Irradiation of the doublet signals at δ_H 3.38 and 3.47 ascribed to the methylene protons enhances the intensities of the double-doublet signals at δ_H 6.95 and 6.08, respectively. Either of the latter signals shows the coupling constants of 15 and 11 Hz, indicating the presence of two vicinal protons which are *trans* and s-*trans* to the proton in question, respectively. This partial information allows the tentative assignment of the 'mono-*cis*' geometry **6a** for this isomer.

X-Ray crystallographic analysis

X-Ray crystallographic analysis was made for the two isomeric thia[21]annulenes **4a** and **4b** since they afforded crystals suitable for the analysis. The perspective drawings of these two compounds are given in Fig. 5. Compound **4a** adopts a conformation with C_2 symmetry and the two methano bridges are in the *anti* arrangement; this conformation was shown to correspond to the minor isomer in solution as shown above. Crystals of compound **4b** contain two independent molecules with very similar structure and one of them is shown in Fig. 5. The final R and R_w values are insufficiently good to discuss the molecular structure in any detail. Nevertheless the *syn* arrangement of the two methano bridges might be safely concluded.

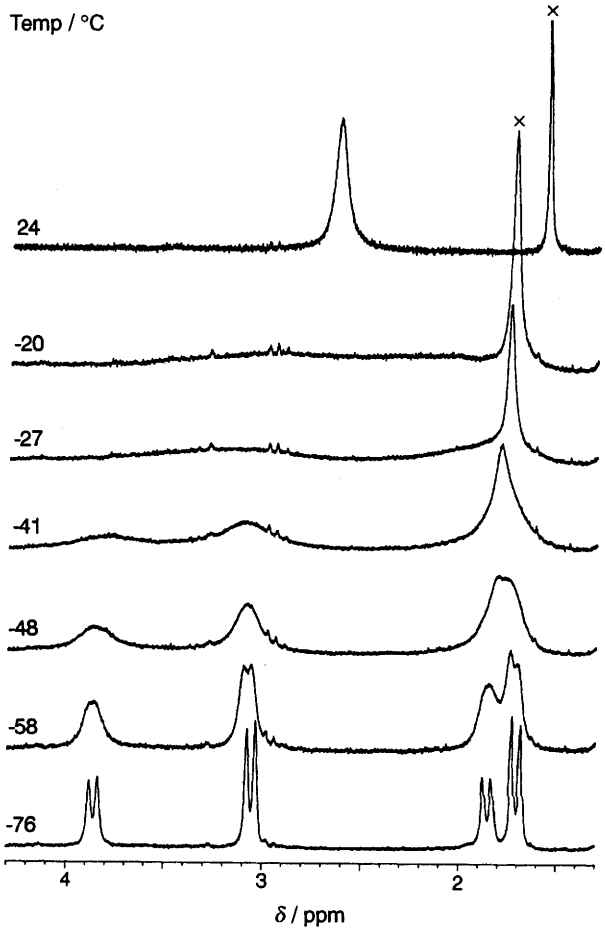


Fig. 2 Temperature dependence of the methylene proton signals of compound **4b**. Peaks with × are due to water.

Tropicity of compounds 4–6

We assume that tropicity of these annulenes can be judged by comparison of the proton chemical shifts with those of the corresponding acyclic precursors chosen as the respective reference compounds. As for the thia[21]annulene, the *syn* conformer of the 'di-*trans*' isomer **4a** shows the upfield shifts of the inner olefinic proton H^A (0.8 ppm) and the methylene protons (0.7 ppm on the average) and the downfield shift of the outer

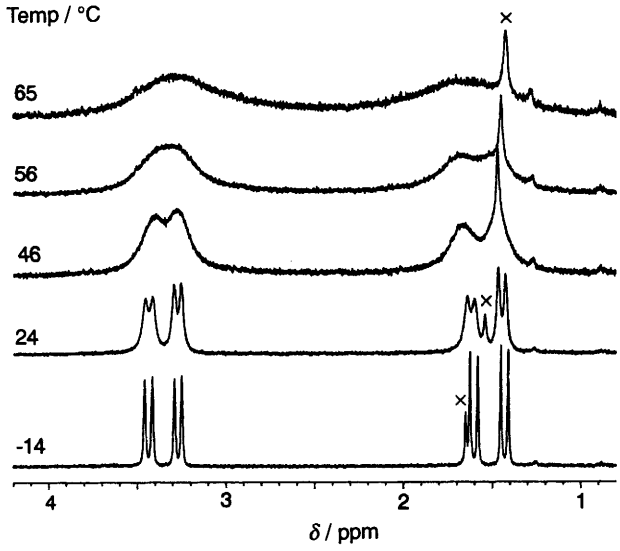


Fig. 3 Temperature dependence of the methylene proton signals of compound **5a**. Peaks with × are due to water.

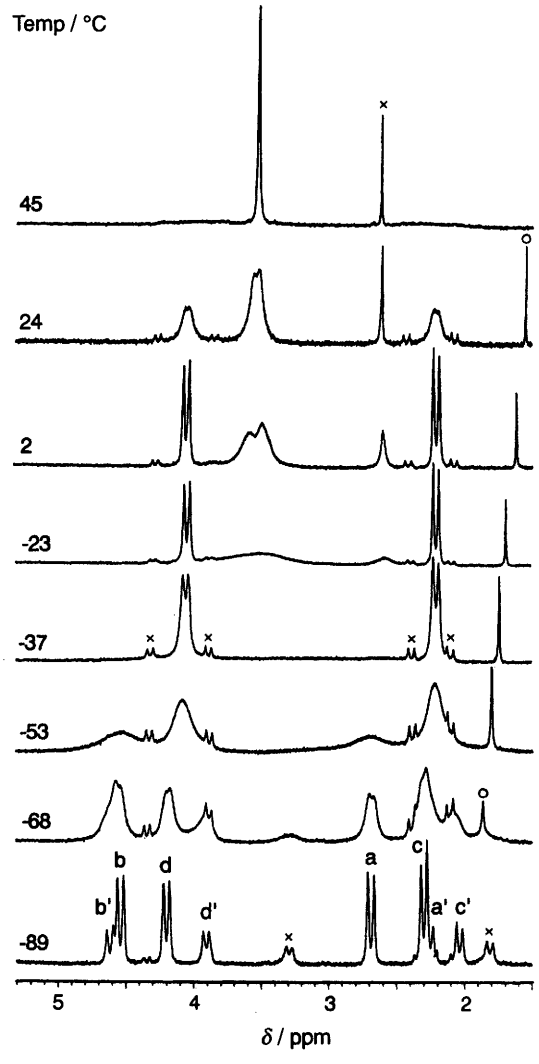
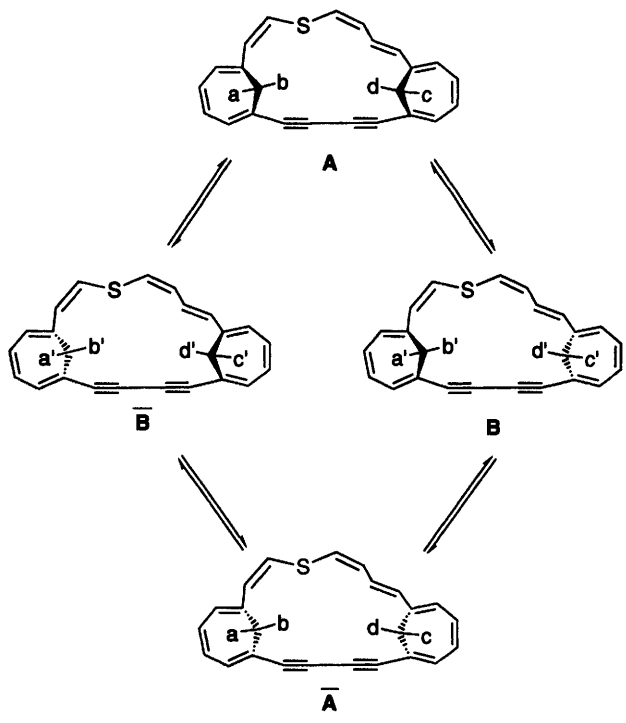


Fig. 4 Temperature dependence of the methylene proton signals of compound **5b**. In CD_2Cl_2 at −89 °C and in $CDCl_3$ at the other temperatures. Signals with × are due to unidentified impurities and that with O is due to water.

olefinic proton H^B (0.28 ppm) relative to the corresponding protons of the reference compound **9a** (see Experimental section for the detailed chemical-shift data). This clearly indicates that



Scheme 4

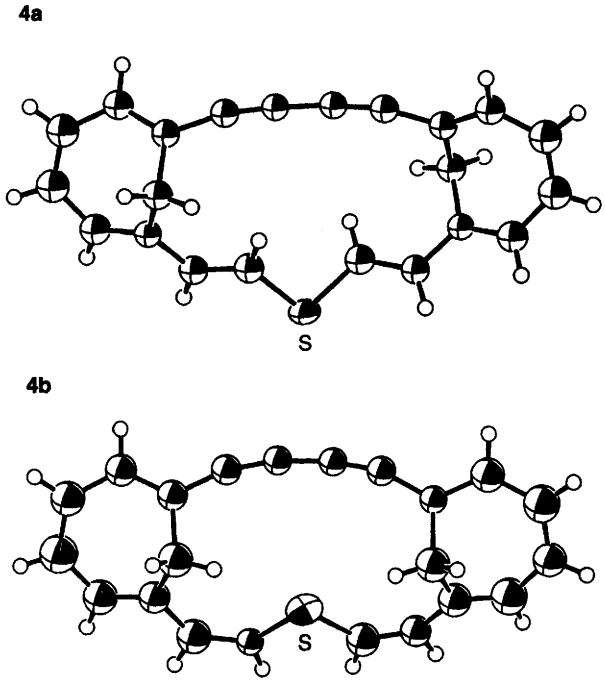


Fig. 5 Perspective drawings of X-ray molecular structures of **4a** and **4b**

this conformer shows diatropicity as expected for the potential 22π-electron system with the participation of the lone pair electrons of the sulfur atom. On the other hand, the *anti* conformer is concluded to be atropic. The difference in diatropicity between *syn*-**4a** and *anti*-**4a** may be ascribed to the difference in the planarity of the peripheral π-system. The trend shown by the *syn* isomer, better planarity and higher tropicity than the corresponding *anti* isomer, has generally been observed in bismethano-bridged annulene derivatives such as the dimethano[14]annulene[15] and the corresponding dimethano-bridged tetradehydro[21]annulenone **13**.[14] As for the thia[23]annulene, the 'di-*cis*' isomer **5b** shows an upfield

shift for the outer olefinic protons (0.5–0.05 ppm) and downfield shifts for the methylene protons (0.78 ppm on the average for the major isomer and 0.41 ppm for the minor isomer) and the inner olefinic proton $H^{C'}$ (~1.0 ppm) relative to the corresponding protons of the reference compound **11b** (see Experimental section for the chemical-shift data). This clearly indicates that the isomer **5b** shows paratropicity as expected for the potential 24π-electron system. Comparison of the ^{1}H NMR data for the isomers ***4b***, **5a**, **6a** and **6b** with those of their corresponding acyclic precursors indicates that these isomers are atropic.

Diatropicity in the dimethanothia[21]annulene **4a** is clearly smaller than that in the monocyclic dimethylthia[21]annulene (**2**; $m = n = 2$)[8] carrying the same number of peripheral π-electrons, as judged by the chemical-shift differences between the inner and outer olefinic proton signals. The similar reduction of paratropicity is observed on going from the dimethanothia[23]annulene **5b** to the monocyclic dimethylthia[23]annulene (**2**; $m = 2$, $n = 3$)[8] with the same peripheral, 24π-electrons from comparison of the chemical-shift data between them.

In conclusion, the tetradehydrodimethanothiaannulenes, **4**, **5** and **6** were found to show no ring-current effect, except for *syn*-**4a** and **5b**. The presence of two methano-bridges therefore helps to decrease the planarity of the peripherally conjugated system. This means that the molecular skeleton of the monocyclic thiaanulenes **2** is sufficiently rigid and planar for tropicity to be fully manifested in these compounds. This conclusion discouraged us from preparing dimethanothiaannulenes larger than compound **6**, since we predict that they would show no ring current effect.

Electronic spectra of compounds 4–6

As described in the discussion of the NMR spectra only compounds **4a** and **5b** show the ring-current effect; compound **6** does not. Also, since each of the compounds **4**–**6** has a different conformation it is difficult to discuss their UV–visible spectral data systematically (see Experimental section).

Experimental

Mps were determined on a hot-stage apparatus and are uncorrected. IR spectra were taken with a JASCO-7300 spectrophotometer as KBr discs, unless otherwise specified; only significant maxima are described. Electronic (UV–visible) spectra were measured in THF solution with a Shimadzu 2200A spectrophotometer. Mass spectra were recorded with a JEOL JMS-D 300 spectrometer operating at 75 eV using a direct-inlet system. Fast atom bombardment mass spectra (FAB MS) were obtained from a *m*-nitrobenzyl alcohol matrix on a JEOL JMS-AX 505W high-resolution double-focusing mass spectrometer equipped with a D 5000 data system. ^{1}H NMR spectra at ambient temperature were recorded as $CDCl_3$ solutions, unless otherwise specified, with a Bruker AM-300 (300 MHz) or a JEOL GX-400 (400 MHz) spectrometer, internal $SiMe_4$ (TMS) being used as internal standard. *J* Values are given in Hz. ^{13}C NMR spectra were recorded for $CDCl_3$ solutions, on an AM-300 or a GX-400 at 75.47 or 100.40 MHz with internal $SiMe_4$ as a reference; in the assignments s = secondary carbon, t = tertiary carbon and q = quaternary carbon.

All the Wittig reactions were carried out under an argon atmosphere. Progress of all reactions was followed by TLC on Merck pre-coated silica gel. Alumina (Merck, activity II–III) was used for column chromatography. Compounds were pre-adsorbed from diethyl ether or benzene solution onto the adsorbent before column chromatography. DMF was dried by stirring it with calcium hydride overnight and then distilling it before use. Organic extracts were washed with saturated aq. sodium chloride and dried over anhydrous sodium sulfate prior to removal of solvent. Solvents were evaporated under water-pump pressure. Ether refers to diethyl ether.

Isomeric 1,5-bis(6-ethynylcyclohepta-1,3,5-trienyl)-3-thiapenta-1,4-dienes 9a, 9b and 9c

A solution of lithium ethoxide prepared from lithium (53 mg, 7.76 mmol) in dry ethanol (19 cm^3) was added dropwise during 2.5 h to a stirred solution of 6-ethynylcyclohepta-1,3,5-triene-1-carbaldehyde **8**[12] (1.00 g, 6.94 mmol) and bis[(triphenylphosphonio)methyl]sulfide dibromide **7**[11] (2.58 g, 3.47 mmol) in dry DMF (200 cm^3) at 60 °C. After being stirred for a further 4 h at 60 °C, the mixture was cooled to room temperature, poured onto water and extracted with benzene. The combined extracts were washed successively with water and brine and dried. The brown semi-solid obtained after removal of the solvent was chromatographed on alumina (5.2 × 8.0 cm). The initial fractions eluted with 5% ether in hexane afforded the 'di-*trans*' *isomer* **9a** (41 mg, 3.8%) of the acyclic sulfide as yellow needles, mp 81–83 °C (from hexane–ether); *m/z* 314 (M^+, 26%) and 171 (100) ($C_{22}H_{18}S$ requires *M*, 314.4); λ_{max}/nm 237 (ε/dm^3 mol^{-1} cm^{-1} 50 700), 262sh (31 200) and 397 (23 500); ν_{max}/cm^{-1} 3285 (C≡CH), 2085 (C≡C), 1597, 1588 (C=C), and 950 [(*E*)-HC=CH]; δ_H(300 MHz) 6.719 (2 H, d, *J* 15.3, H^A), 6.660 (2 H, dd, *J* 10.9 and 6.2, H^2), 6.587 (2 H, d, *J* 6.0, H^4), 6.512 (2 H, dd, *J* 10.8 and 6.1, H^3), 6.486 (2 H, d, *J* 15.3, H^B), 6.158 (2 H, d, *J* 6.1, H^1), 2.867 (2 H, s, C≡CH) and 2.684 (4 H, s, CH_2); δ_C(75.47 MHz) 132.62 (t), 132.07 (t), 131.14 (t), 130.19 (q), 129.18 (t), 125.11 (t), 123.67 (t), 112.76 (q), 85.82 (q, –C≡), 74.35 (t, ≡CH) and 33.12 (s, CH_2) (Found: C, 83.95; H, 6.0. $C_{22}H_{18}S$ requires C, 84.0; H, 5.8%).

The following fractions eluted with 7% ether in hexane afforded the 'mono-*cis*' *isomer* **9b** (121 mg, 11.1%) as an unstable liquid; *m/z* 314 (M^+, 2%) and 57 (100) ($C_{22}H_{18}S$ requires *M*, 314.4); λ_{max}/nm 243.5 (ε 49 800), 268sh (38 500) and 391 (37 100); ν_{max}/cm^{-1} 3288 (C≡CH), 2085 (C≡C), 1590, 1557 (C=C), 939 [(*E*)-HC=CH] and 739 [(*Z*)-HC=CH]; δ_H(300 MHz) 6.696 (1 H, dd, *J* 11.0 and 6.3, $H^{2'}$), 6.658 (1 H, d, *J* 15.3, H^A), 6.648 (1 H, dd, *J* 11.0 and 6.0, H^2), 6.582 (1 H, dq, *J* 6.3 and 0.5, H^4 or $H^{4'}$), 6.574 (1 H, dq, *J* 6.3 and 0.5, $H^{4'}$ or H^4), 6.506 (1 H, dd, *J* 10.9 and 6.1, $H^{3'}$), 6.500 (1 H, dd, *J* 10.9 and 6.1, H^3), 6.437 (1 H, dd, *J* 15.3 and 0.5, H^B), 6.420 (1 H, d, *J* 10.5, $H^{A'}$), 6.393 (1 H, d, *J* 5.5, $H^{1'}$), 6.154 (1 H, d, *J* 5.4, H^1), 6.144 (1 H, d, *J* 11.1, $H^{B'}$), 2.849 (1 H, s, C≡CH), 2.841 (1 H, s, C≡CH), 2.732 (2 H, s, CH_2) and 2.647 (2 H, s, CH_2); δ_c(75.47 MHz) 132.68 (t), 132.64 (t), 132.05 (t), 131.95 (t), 130.50 (t), 130.02 (q), 129.19 (t), 129.17 (t), 129.03 (q), 127.50 (t), 126.81 (t), 126.49 (t), 126.03 (t), 125.25 (t), 112.76 (q), 85.82 (q, –C≡), 85.75 (q, –C≡), 74.62 (t, ≡CH), 74.36 (t, ≡CH), 37.62 (s, CH_2) and 32.96 (s, CH_2).

The later fractions eluted with 10% ether in hexane afforded the 'di-*cis*' isomer **9c** (123 mg, 10.3%) as a liquid; *m/z* 314.1114 ($C_{22}H_{18}S$ requires *M*, 314.1126); λ_{max}/nm 236 (ε 43 800), 256.5sh (32 200) and 385.5 (21 400); ν_{max}/cm^{-1} 3289 (C≡CH), 2086 (C≡C), 1554 (C=C) and 742 [(*Z*)-HC=CH]; δ_H(300 MHz) 6.692 (2 H, dd, *J* 10.9 and 6.3, H^2), 6.575 (2 H, dq, *J* 6.1 and 0.6, H^4), 6.501 (2 H, dd, *J* 10.9 and 6.1, H^3), 6.424 (2 H, d, *J* 6.3, H^1), 6.262 (2 H, d, *J* 10.7, H^A), 6.086 (2 H, d, *J* 10.7, H^B), 2.828 (2 H, s, C≡CH) and 2.755 (4 H, s, CH_2); δ_C(75.47 MHz) 132.75 (t), 132.04 (t), 129.25 (t), 129.17 (q), 128.36 (t), 127.06 (t), 126.99 (t), 112.41 (q), 85.80 (q, –C≡), 74.84 (t, ≡CH) and 37.33 (s, CH_2).

Isomeric 7,8,9,10-tetradehydro-1,6:11,16-dimethano-19-thia-[21]annulenes 4a and 4b

A solution of a mixture of compounds **9a**, **9b** and **9c** (300 mg, 0.96 mmol) in pyridine (45 cm^3) and ether (15 cm^3) was added dropwise during 3 h to a stirred solution of anhydrous copper(II) acetate (1.22 g, 6.72 mmol) in pyridine (30 cm^3) and ether (10 cm^3) at 45–47 °C. The mixture was stirred for 2 h at 45 °C and then poured onto water and extracted with benzene. The combined extracts were washed repeatedly with 1 mol dm^{-3} hydrochloric acid until they turned acidic, and then with aq. $NaHCO_3$. The residue obtained after removal of the solvent

was chromatographed on alumina (2.0 × 7.0 cm). The initial fractions eluted with 1% ether in hexane afforded the 'di-*trans*' *isomer* **4a** (124 mg, 42%) of the thia[21]annulene as yellow needles, mp 219–222 °C (decomp.) (from hexane–benzene); *m/z* 312 (M^+, 100%) ($C_{22}H_{16}S$ requires *M*, 312.4); δ_{max}/nm 240.5 (ε 35 300), 278 (26 300), 290.5 (28 000), 341.5 (29 000) and 442.5sh (4300); ν_{max}/cm^{-1} 2165 (C≡C), 1589 (C=C) and 932 [(*E*)-HC=CH]; the ^{1}H NMR spectrum showed the presence of two conformers, *syn* and *anti*, in a ratio ~3:1. *syn*-**4a**: δ_H(300 MHz) 6.943 (2 H, dd, *J* 10.9 and 6.1, H^2), 6.778 (s H, dd, *J* 10.9 and 6.1, H^3), 6.714 (2 H, d, *J* 15.4, H^B), 6.677 (2 H, d, *J* 6.0, H^4) 6.324 (2 H, d, *J* 6.0, H^1), 5.924 (2 H, d, *J* 15.4, H^A), 2.968 (2 H, d, *J* 12.5, H^b) and 1.222 (2 H, d, *J* 12.6, H^a); δ_C(75.47 MHz) 132.74 (t), 130.25 (t), 129.72 (t), 128.86 (t), 128.65 (t), 125.23 (q), 123.31 (t), 109.24 (q), 88.24 (q, –C≡), 73.34 (q, –C≡) and 34.68 (s, CH_2). *anti*-**4a**: δ_H(300 MHz) 6.779 (2 H, dd, *J* 10.9 and 6.1, H^2), 6.625 (2 H, dd, *J* 10.9 and 6.0, H^3), 6.588 (2 H, d, *J* 15.0, H^B), 6.543 (2 H, d, *J* 15.0, H^A), 6.540 (2 H, d, *J* 6.0, H^4), 6.239 (2 H, d, *J* 5.7, H^1), 3.369 (2 H, d, *J* 12.5, H^b) and 1.650 (2 H, d, *J* 12.7, H^a); δ_C(75.47 MHz) 132.67 (t), 132.46 (t), 129.67 (t), 129.14 (t), 128.93 (q), 125.30 (t), 124.07 (t), 110.58 (q), 85.84 (q, –C≡), 72.78 (q, –C≡) and 34.43 (s, CH_2) (Found: C, 84.6; H, 5.3. $C_{22}H_{16}S$ requires C, 84.6; H, 5.2%).

The later fractions eluted with 2–5% ether in hexane afforded the 'di-*cis*' *isomer* **4b** (35 mg, 12%) as red needles, mp 170–173 °C (decomp.) (from hexane–benzene); *m/z* 312 (M^+, 100%) ($C_{22}H_{16}S$ requires *M*, 312.4); λ_{max}/nm 237 (ε 43 500), 240sh (42 300), 276 (34 600), 292 (31 600), 352.5 (29 200) and 440sh (4800); ν_{max}/cm^{-1} 2156 (C≡C), 1579, 1552 (C=C), and 698 [(*Z*)-HC=CH]; δ_H(400 MHz) 6.759 (2 H, dd, *J* 11.1 and 6.5, H^2), 6.671 (2 H, dd, *J* 11.1 and 6.2, H^3), 6.591 (2 H, d, *J* 6.2, H^4), 6.484 (2 H, d, *J* 11.4, H^A), 6.433 (2 H, d, *J* 6.5, H^1), 6.294 (2 H, d, *J* 11.4, H^B) and 2.629 (4 H, br s, CH_2); δ_H(300 MHz, –76 °C) the major isomer: 3.056 (1 H, d, *J* 13), 1.704 (1 H, d, *J* 13); the minor isomer: 3.861 (1 H, d, *J* 13), 1.852 (1 H, d, *J* 13); δ_C(100.4 MHz) 131.69 (t), 129.99 (t), 129.81 (q), 129.20 (t), 128.65 (t), 127.97 (t), 126.64 (t), 111.73 (q), 95.91 (q, –C≡), 77.55 (q, –C≡) and 35.98 (s, CH_2) (Found: C, 84.3; H, 5.6. $C_{22}H_{16}S$ requires C, 84.6; H, 5.2%).

Isomeric 1,7-bis(6-ethynylcyclohepta-1,3,5-trienyl)-3-thiahepta-1,4,6-trienes 11a and 11b

A solution of lithium ethoxide prepared from lithium (66 mg, 9.6 mmol) in dry ethanol (22 cm^3) was added dropwise during 2 h to a stirred solution of the aldehyde **8**[12] (677 mg, 4.70 mmol), the aldehyde **10**[12] (800 mg, 4.70 mmol) and the salt **7**[11] (3.50 g, 4.70 mmol) in dry DMF (268 cm^3) at 67–68 °C. After being stirred for a further 3.5 h at 67–68 °C, the mixture was worked up as for the isolation of compound **9a**. The product was chromatographed on alumina (4.2 × 5.0 cm). The initial fractions eluted with 10–20% benzene in hexane afforded compound **11a** together with its stereoisomers and compound **12a** together with its stereoisomers. The following fractions eluted with 30–50% benzene in hexane afforded compounds **9a** and **12a** and their stereoisomers. The pale yellow liquid obtained after evaporation of the initial fractions was again chromatographed on alumina (3.2 × 4.0 cm). The fractions eluted with 30–40% benzene in hexane were collected and evaporated. The residual liquid was subjected to PLC (hexane–benzene; 3:1). The fast-moving, first band afforded *compound* **11a** (65 mg, 4.1%) as a pale yellow liquid; *m/z* 340 (M^+, 5%) and 57 (100) ($C_{24}H_{20}S$ requires *M*, 340.4); λ_{max}/nm 239.5 (ε 14 500), 261sh (12 700), 278sh (11 200) and 402.5 (9480); ν_{max}/cm^{-1} 3285 (C≡CH), 2088 (C≡C), 1601 (C=C), 976 [(*E*)-HC=CH] and 743 [(*Z*)-HC=CH]; δ_H(400 MHz) 6.694 (1 H, d, *J* 15.4, $H^{D'}$),6.71–6.62 (3 H, m, H^2 or $H^{2'}$, H^3 or $H^{3'}$, and $H^{B'}$), 6.587 (1 H, d, *J* 5.6, H^1 or $H^{1'}$ or H^4 or $H^{4'}$), 6.580 (1 H, d, *J* 5.9, $H^{1'}$ or H^4 or $H^{4'}$ or H^1), 6.53–6.50 (3 H, m, $H^{2'}$ or H^2, H^2 or H^3, $H^{2'}$ or H^3, and $H^{C'}$), 6.500 (1 H, d, *J* 10.8, H^A or H^B), 6.484 (1 H, d, *J* 11.5, H^B or H^A), 6.294 (1 H, d, *J* 15.1, $H^{A'}$), 6.230 (1 H, d, *J* 6.3, H^4 or $H^{4'}$ or H^1 or $H^{1'}$), 6.176 (1 H, d, *J* 6.3, $H^{4'}$ or H^1 or $H^{1'}$ or H^4), 2.865 (1 H, s, C≡CH 2.853 (1 H, s, C≡CH), 2.700 (2 H, s, CH_2) and 2.681 (2 H, CH_2).

The fast moving, third band afforded *compound* **11b** (82 mg 5.1%) as a pale yellow liquid; no satisfactory mass spectra could be obtained by the direct-inlet method; λ_{max}/nm 239 (ε 12 300, 263.5sh (10 300) and 397.5 (7860); ν_{max}/cm^{-1} 3290 (C≡CH), 2086 (C≡C), 1599 (C=C), 973 [(*E*)-HC=CH] and 740 [(*Z*)-HC=CH]; δ_H(400 MHz) 6.698 (1 H, dd, *J* 11.0 and 6.1, H^2 or $H^{2'}$ or H^3 or $H^{3'}$), 6.646 (1 H, dd, *J* 11.2 and 6.3, $H^{2'}$ or H^3 or $H^{3'}$ or H^2), 6.632 (1 H, d, *J* 6.3, H^1 or H^4 or $H^{4'}$), 6.581 (1 H, d, *J* 5.9 H^4 or $H^{4'}$ or H^1), 6.575 (1 H, d, *J* 5.9, $H^{4'}$ or H^1 or H^4), 6.53–6.47 (2 H, m, $H^{2'}$ or H^3 or $H^{3'}$ or H^2), 6.499 (1 H, d, *J* 11.0, $H^{A'}$), 6.42–6.36 (2 H, m, $H^{B'}$ and $H^{C'}$), 6.377 (1 H, d, *J* 11.0, H^A), 6.302 (1 H, d, *J* 15.1, $H^{D'}$), 6.230 (1 H, d, *J* 6.3, $H^{1'}$), 6.125 (1 H, d, *J* 10.5, H^B), 2.843 (1 H, s, C≡CH), 2.837 (1 H, s, C≡CH), 2.723 (2 H, s, CH_2) and 2.687 (2 H, s, CH_2).

The fast moving, fourth band afforded a pale yellow liquid (10 mg), the identification of which was precluded by its thermal instability and low yield.

Isomeric 7,8,9,10-tetradehydro-1,6:11,16-dimethano-19-thia[23]annulenes 5a and 5b

A solution of compounds **11a** and **11b** (320 mg, 0.94 mmol) in pyridine–ether (3:1; 76 cm^3) was added dropwise during 3 h to a stirred solution of anhydrous copper(II) acetate (2.56 g, 14.1 mmol) in pyridine–ether (3:1; 76 cm^3) at 50–53 °C and the mixture was stirred for a further 1.5 h at 50–53 °C. The mixture was worked up as for the isolation of compound **4a**. The product was chromatographed on alumina (3.8 × 4.5 cm). The initial fractions eluted with 15% ether in hexane afforded the 'mono-*cis*' *isomer* **5a** (43 mg, 14%) of the thia[23]annulene as yellow needles, mp 231–233 °C (decomp.) (from hexane–benzene); *m/z* 338 (M^+, 74%) and 28 (100) ($C_{24}H_{18}S$ requires *M*, 338.4); λ_{max}/nm 253 (ε 35 300), 279 (57 000) and 362sh (16 800); ν_{max}/cm^{-1} 2176 (C≡C), 1597, 1587 (C=C), 973 [(*E*)-HC=CH] and 724 [(*Z*)-HC=CH]; δ_H(300 MHz, –33 °C) 7.050 (1 H, dd, *J* 14.8 and 10.7, $H^{C'}$), 6.950 (1 H, dd, *J* 10.7 and 8.1, $H^{B'}$), 6.86–6.62 (8 H, m, olefinic and 7-membered ring H), 6.455 (1 H, d, *J* 6.2, 7-membered ring H), 6.372 (1 H, d, *J* 15.4, H^A), 6.281 (1 H, d, *J* 6.1, 7-membered ring H), 6.215 (1 H, d, *J* 8.1, $H^{A'}$), 3.436 (1 H, d, *J* 12.5, H^d), 3.269 (1 H, d, *J* 12.3, H^b), 1.594 (1 H, d, *J* 12.7, H^c) and 1.422 (1 H, d, *J* 12.4, H^a); δ_C(75.47 MHz, –33 °C) 142.76 (t), 137.18 (t), 132.40 (t), 132.35 (t), 132.09 (t), 130.93 (t), 130.38 (q), 130.14 (t), 129.92 (t), 129.74 (t), 128.34 (t), 127.75 (t), 126.79 (q), 125.86 (t), 123.95 (t), 119.28 (t), 111.30 (q), 109.41 (q), 84.34 (q, –C≡), 83.69 (q, –C≡), 71.59 (q, –C≡), 71.22 (q, –C≡), 33.29 (s, CH_2) and 32.21 (s, CH_2) (Found: C, 84.8; H, 5.5. $C_{24}H_{18}S$ requires C, 85.2; H, 5.4%).

The later fractions eluted with 20% ether in hexane afforded the 'di-*cis*' *isomer* **5b** (37 mg, 12%) as red needles, mp 204–207 °C (decomp.) (from hexane–benzene); *m/z* 338 (M^+, 100%) ($C_{24}H_{18}S$ requires *M*, 338.4); λ_{max}/nm 232 (ε 32 300), 248 (30 500), 274 (21 300), 295sh (32 600), 311 (39 400), 327 (39 000) and 381.5sh (12 900); ν_{max}/cm^{-1} 2179 (C≡C), 1592, 1580 (C=C), 963 [(*E*)-HC=CH] and 709 [(*Z*)-HC=CH]; δ_H(300 MHz) 7.540 (1 H, dd, *J* 15.2 and 10.8, $H^{C'}$), 6.64–6.30 (7 H, m, 7-membered ring H), 6.254 (1 H, d, *J* 15.2, $H^{D'}$), 6.13 (1 H, dd, 7-membered ring H), 6.127 (1 H, dd, *J* 11.2 and 9.4, $H^{B'}$), 6.041 (1 H, d, *J* 11.8, H^A or H^B), 6.000 (1 H, d, *J* 9.5, $H^{A'}$), 5.936 (1 H, d, *J* 11.1, H^B or H^A), 3.999 (1 H, br s, CH_2), 3.502 (2 H, br s, CH_2) and 2.195 (1 H, br s, CH_2); δ_H(300 MHz, CD_2Cl_2, –89 °C, the olefinic proton signals are omitted) and major isomer: 4.538 (1 H, d, *J* 13.6), 4.200 (1 H, d, *J* 12.8), 2.687 (1 H, d, *J* 13.8), 2.300 (1 H, d, *J* 12.7); the minor isomer 4.615 (1 H, d, *J* 14.3), 3.908 (1 H, d, *J* 13.0), 2.255 (1 H, d, *J* 14) and 2.037 (1 H, d, *J* 12.7): δ_C(75.47 MHz) 133.96 (t), 132.92 (t), 132.67 (t), 132.52 (t), 131.44 (q), 131.18 (q), 130.19 (t), 130.14 (t), 129.72 (t), 129.62 (t), 127.67 (t), 127.64 (t), 127.53 (t), 126.11 (t), 125.57 (t), 124.69 (t), 113.87 (q), 113.76 (q), 85.80 (q, –C≡), 85.01 (q,

Table 1 Crystallographic data for compounds **4a** and **4b**

	4a	**4b**
Empirical formula	$C_{22}H_{16}S$	$C_{22}H_{16}S$
Formula weight	312.43	312.43
Crystal dimension (mm)	0.20 × 0.15 × 0.15	0.40 × 0.15 × 0.08
Space group	$P2_12_12$ (No. 18)	$P\bar{1}$ (No. 2)
Lattice parameter		
a/Å	14.459(12)	8.067(3)
b/Å	4.275(4)	26.113(13)
c/Å	13.145(4)	8.101(2)
α/°	90.0	96.00(5)
β/°	90.0	103.11(2)
γ/°	90.0	95.79(2)
V/Å^3	813(2)	1620(1)
Z	2	4
D_{calc} g cm^{-3}	1.277	1.265
F_{000}	328	656
μ(Mo–Kα)/cm^{-1}	1.86	1.86
Scan width (°)	1.31 + 0.30 tan θ	0.73 + 0.30 tan θ
$2\theta_{max}$/°	55.0	50.0
No. of reflections measured	1155	4806
No. of unique reflections measured	1155	4367
p-Factor	0.01	0.04
No. observations	378 [$I > 2.5\sigma(I)$]	956 [$I > 2.0\sigma(I)$]
No. variables	50	195
Reflection/parameter ratio	7.56	4.90
Residuals: R(R_w)	0.054 (0.040)	0.095 (0.094)
Goodness of fit indicator (GOF)	1.62	1.94
Max shift/error in final diff. map	0.31	0.39
Peak$_{max}$ in final diff. map (e Å^{-3})	0.25	0.38
Peak$_{min}$ in final diff. map (e Å^{-3})	−0.22	−0.35

–C≡), 74.11 (q, –C≡), 74.09 (q, –C≡), 36.89 (s, CH_2) and 32.69 (s, CH_2) (Found: C, 85.0; H, 5.4. $C_{24}H_{18}S$ requires C, 85.2; H, 5.4%).

Isomeric 1,9-bis(6-ethynylcyclohepta-1,3,5-trienyl)-5-thianona-1,3,6,8-tetraenes 12a, 12b and 12c

A solution of lithium ethoxide prepared from lithium (22 mg, 3.23 mmol) in dry ethanol (8 cm^3) was added dropwise during 2 h to a stirred solution of the aldehyde **10**[12] (550 mg, 3.23 mmol) and the salt **7**[11] (1.20 g, 1.62 mmol) in dry DMF (93 cm^3) at 62–67 °C. After being stirred for a further 3 h at 65–67 °C, the mixture was worked up as for the isolation of compound **9a**. The product was chromatographed on alumina (4.3 × 6.0 cm). The initial fractions eluted with 15% ether in hexane afforded the 'all-*trans*' *isomer* **12a** (70 mg, 11.8%) as red–brown needles, mp 104–108 °C (decomp.) (from hexane–benzene); *m/z* 366 (M^+) (FAB method) ($C_{26}H_{22}S$ requires M, 366.4); λ_{max}/nm 249.5 (ε 45 200), 271sh (42 900), 284.5sh (34 800) and 416.5 (42 200); ν_{max}/cm^{-1} 3295 (C≡H), 2086 (C≡C), 1597, 1544 (C=C), and 970 [(*E*)-HC=CH]; δ_H(300 MHz, [$^2H_6$]benzene) 6.628 (2 H, dd, J 15.3 and 10.5, H^C or H^B), 6.548 (2 H, d, J 6.0, H^4 or H^1), 6.399 (2 H, dd, J 11.1 and 6.3, H^2 or H^3), 6.259 (2 H, dd, J 14.8 and 10.7, H^B or H^C), 6.203 (2 H, dd, J 11.1 and 6.1, H^3 or H^2), 6.064 (2 H, d, J 14.8, H^A or H^D), 6.033 (2 H, d, J 15.0, H^D or H^A), 5.997 (1 H, d, J 6.4, H^1 or H^4), 2.753 (4 H, s, CH_2) and 2.530 (2 H, s, C≡CH); δ_C(75.47 MHz) 132.78 (t), 132.48 (t), 132.16 (t), 131.79 (q), 131.14 (t), 129.16 (t), 129.11 (t), 126.62 (t), 125.90 (t), 112.96 (q), 85.83 (q, –C≡), 74.33 (t, ≡CH) and 32.83 (s, CH_2) (Found: C, 84.9; H, 6.1. $C_{26}H_{22}S$ requires C, 85.2; H, 6.0%).

The following fractions eluted with 20% ether in hexane afforded the 'mono-*cis*' *isomer* **12b** (90 mg, 15%) as a red liquid; no satisfactory mass spectra could be obtained by the direct-inlet or FAB methods; λ_{max}/nm 237.5 (ε 22 500), 274.5 (14 300) and 414 (9650); ν_{max}/cm^{-1} 3311 (C≡CH), 1601, 1581 (C=C), 963 [(*E*)-HC=CH] and 706 [(*Z*)-HC=CH]; δ_H(300 MHz) 6.869 (1 H, dd, J 15.2 and 11.2, H^B or H^C or $H^{C'}$), 6.696–6.208 (15 H, m, olefinic and 7-membered ring H), 2.920 (1 H, s, C≡CH), 2.840 (1 H, s, C≡CH), 2.708 (2 H, s, CH_2) and 2.694 (2 H, s, CH_2).

The later fractions eluted with 25% ether in hexane afforded the 'di-*cis*' *isomer* **12c** (102 mg, 17.2%) as a red liquid; no satisfactory mass spectra could be obtained by the direct-inlet or FAB methods; δ_{max}/nm 249.5 (ε 12 900), 278.5 (10 300), 339.5 (6000) and 378 (5900); ν_{max}/cm^{-1} 3302 (C≡CH), 964 [(*E*)-HC=CH] and 741 [(*Z*)-HC=CH]; δ_H(300 MHz) 6.880 (2 H, dd, J 15.2 and 10.7, H^C), 6.677 (2 H, dd, J 10.8 and 6.3, H^2), 6.598 (2 H, dd, J 6.0 and 0.6, H^4), 6.532 (2 H, dd, J 10.8 and 6.0, H^3), 6.416 (2 H, d, J 15.6, H^D), 6.313 (2 H, dd, J 10.7 and 9.4, H^B), 6.280 (2 H, d, J 6.1, H^1), 6.214 (2 H, d, 9.3, H^A), 2.995 (2 H, s, C≡CH) and 2.732 (4 H, s, CH_2); δ_C(75.47 MHz) 134.43 (t), 132.41 (t), 132.01 (t), 131.63 (q), 129.46 (t), 127.85 (t), 126.74 (t), 125.82 (t), 125.57 (t), 113.26 (q), 85.84 (q, –C≡), 74.69 (t, ≡CH) and 33.27 (s, CH_2).

Isomeric 7,8,9,10-tetradehydro-1,6:11,16-dimethano-21-thia[25]annulenes 6a and 6b

A solution of a mixture of compounds **12a**, **12b** and **12c** (160 mg, 0.44 mmol) in pyridine–ether (3:1; 44 cm^3) was added dropwise during 3.5 h to a stirred solution of anhydrous copper(II) acetate (1.22 g, 6.72 mmol) in pyridine–ether (3:1; 35 cm^3) at 52–55 °C after which the mixture was stirred for a further 1.5 h at 52–55 °C. The mixture was worked up as for the isolation of compound **4a**. The product was chromatographed on alumina (3.2 × 4.0 cm). The initial fractions eluted with 10% ether in hexane afforded the 'mono-*cis*' *isomer* **6a** (20 mg, 12.6%) of the thia[25]annulene as orange needles, mp 208–211 °C (decomp.) (from hexane–benzene); *m/z* 364 (M^+, 100%) ($C_{26}H_{20}S$ requires M, 364.4); λ_{max}/nm 243.5 (ε 34 700), 293.5 (68 400), 322sh (31 700) and 365sh (23 200); ν_{max}/cm^{-1} 2183 (C≡C), 1590 (C=C), 966 [(*E*)-HC=CH] and 710 [(*Z*)-HC=CH]; δ_H(300 MHz) 6.946 (1 H, dd, J 15.2 and 11.0, olefinic H), 6.796–6.257 (15 H, m, olefinic and 7-membered ring H), 3.469 (1 H, d, J 12.3, H^b), 3.374 (1 H, d, J 13.4, H^d), 2.078 (1 H, d, J 13.3, H^c) and 1.521 (1 H, d, J 12.2, H^a); δ_C(75.47 MHz) 139.34 (t), 138.74 (t), 134.40 (t), 132.50 (t), 132.35 (t), 132.15 (q), 131.62 (t), 130.92 (t), 130.08 (t), 129.99 (t), 129.97 (t), 129.66 (q), 129.48 (t), 128.53 (t), 128.47 (t), 125.02 (t), 124.70 (t), 119.61 (t), 113.08 (q), 110.41 (q), 84.12 (q, –C≡), 83.88 (q, –C≡), 71.94 (q, –C≡), 71.38 (q, –C≡), 33.92 (s, CH_2) and 31.26 (s, CH_2) (Found: C, 86.0; H, 5.55. $C_{26}H_{20}S$ requires C, 85.7; H, 5.5%).

The later fractions eluted with 15% ether in hexane afforded the 'all-*trans*' *isomer* **6b** (16 mg, 10.1%) as red needles, mp 232–234 °C (decomp.) (from hexane–benzene); *m/z* 364 (M^+, 100%) ($C_{26}H_{20}S$ requires *M*, 364.4); λ_{max}/nm 252 (ε 23 100), 295 (31 700), 303sh (30 900), 365 (20 700) and 476sh (3200); ν_{max}/cm^{-1} 2172 (C≡C), 1598 (C=C) and 960 [(*E*)-HC=CH]; δ_H(300 MHz) 6.744 (2 H, dd, *J* 11.1 and 6.3, H^2 or H^3), 6.720 (2 H, d, *J* 6.5, H^4 or H^1), 6.596 (2 H, dd, *J* 11.0 and 6.4, H^3 or H^2), 6.522–6.344 (8 H, m, olefinic H), 6.316 (2 H, d, *J* 6.2, H^1 or H^4) and 2.584 (4 H, s, CH_2); δ_C(75.47 MHz) 133.95 (t), 133.52 (t), 132.43 (t), 131.00 (q), 129.43 (t), 126.65 (t), 126.41 (t), 126.41 (t), 125.71 (t), 113.36 (q), 84.41 (q, –C≡), 72.65 (q, –C≡) and 33.50 (s, CH_2) (Found: C, 85.4; H, 5.9. $C_{26}H_{22}S$ requires C, 85.7; H, 5.5%).

X-Ray crystallography

Crystals of compounds **4a** and **4b** were grown from dichloromethane. Diffraction intensities were measured on a Rigaku AFC-5R diffractometer using graphite monochromated Mo-Kα for **4a** and **4b**. The refined cell parameters and additional relevant crystallographic details for both crystals are summarized in Table 1. The transformation matrix (1 0 1 / 1 0 −1 / 0 1 0) generates a pseudo-monoclinic cell [$a = 9.996(4)$, $b = 12.586(3)$, $c = 26.110(8)$ Å, $\alpha = 89.93(2)$, $\beta = 99.44(3)$, $\gamma = 89.60(3)°$] for **4b**, however, we were unable to find any correlation between the transformed coordinates of the non-H atoms of the two independent molecules. Calculations were performed using the TEXSAN program system.[16] The structures were solved by direct methods. Subsequent full-matrix least-squares refinements were converged with anisotropic and isotropic thermal parameters for S and C atoms, respectively. The minimized functions were $\Sigma\omega(|F_o| - |F_c|)^2$ where $\omega = 4F_o^2/\sigma^2(F_o^2)$. Compound **4a** was found to have crystallographical C_2 symmetry with the S atom on the axis, while **4b** was found to have two crystallographically independent molecules with a *syn*-conformation. The final positional parameters with B_{eq}, the thermal parameters U_{ij}, bond lengths, bond angles, torsion angles and least square planes of **4a** and **4b** have been deposited at the Cambridge Crystallographic Data Centre.†

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