Synthesis and Properties of Dimethyltetradehydrothia-[19]-, -[21]-, -[23]-, and -[25]-annulene. Diatropic and Paratropic Analogues of Thiophene

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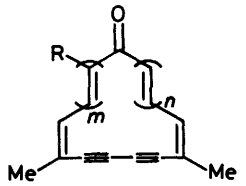
The title thia-annulenes (**9**), (**11**), (**14**), and (**16**) have been synthesized by Wittig reactions of (2*E*,4*Z*)-5-methylhepta-2,4-dien-6-ynal (**6**) and its vinylogous aldehydes (**7**), (**12**) with bis-[(triphenylphosphonio)methyl] sulphide dibromide (**5**), followed by intramolecular oxidative coupling of the resulting acyclic sulphides. The properties of the thia-annulenes are discussed on the basis of ^{1}H NMR and electronic spectra and compared with those of their lower homologues.

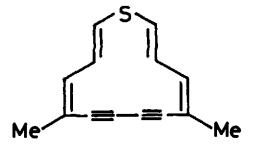
Although diatropicity or paratropicity in monocyclic conjugated systems reduces with increasing ring size,[1] a monocyclic 30-membered annulene, tetradehydro[30]annulene, has been reported to show diatropicity.[2] The degree of dia- or paratropicity of an annulenone or a heteroannulene has been found to be much smaller than that of the corresponding carbocyclic annulene;[3] similarly, benzene, the parent compound of annulenes, is more diatropic than tropone or heteroaromatics such as pyridine, pyrrole, furan, and thiophene. Thus, the limiting ring size to show dia- or para-tropicity is predicted to be smaller for annulenone and heteroannulene systems than the 30-membered ring observed in the carbocyclic annulene system. However, the alternation of the tropic nature between [4*n* + 2]π- and [4*n*]π-electron systems, arising from polarization of carbonyl group of dimethyl- or trimethyltetradehydroannulenones of type (**1**), has been confirmed from 13- to 25-membered ring size.[4,5]

In 1975, Sondheimer and co-workers reported the synthesis of diatropic dimethyltetradehydrothia-[13]- and -[17]-annulene [(**2**)[6] and (**3**)[7] respectively] as well as that of paratropic dimethyltetradehydrothia[15]annulene (**4**);[8] they also described configurational and conformational isomerism in the thia[13]- and thia[17]-annulene systems. These thia-annulenes are formally derived from the tetradehydroannulenones (**1**) by replacement of the carbonyl group with a sulphur atom, and therefore the thia-annulenes showed the reverse tropicity of the dehydroannulenone (**1**) of the same ring size, due to the contribution of the lone pair of electrons of the sulphur atom in the thia-annulene system.[6–8]

We extended their work to the synthesis of tetrahydrothia[19]- (**9**), -thia[21]- (**11**), -thia[23]- (**14**), and -thia[25]-annulene (**16**), in order to compare the tropic nature between the [4*n* + 2]π- and [4*n*]π-systems more systematically and to investigate the limiting size for dia- or para-tropicity in the monocyclic tetradehydrothia-annulene series. Compounds (**9**), (**11**), (**14**), and (**16**) are members of a series of monocyclic thia-annulenes in which the number of double bonds is increased systematically, and hence a study of their spectral properties is particularly informative. The tetradehydro-thia[23]- (**14**) and -thia[25]-annulene (**16**) are the largest monocyclic heteroannulenes so far obtained.[9]



[13] (**1a**) R=H, *m*=*n*=1
[15] (**1b**) R=H, *m*=1, *n*=2
[17] (**1c**) R=H, *m*=*n*=2
[19] (**1d**) R=H, *m*=2, *n*=3
[21] (**1e**) R=H, *m*=*n*=3
[23] (**1f**) R=Me, *m*=3, *n*=4
[25] (**1g**) R=Me, *m*=*n*=4



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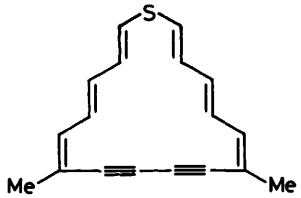

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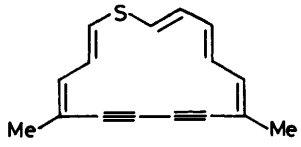


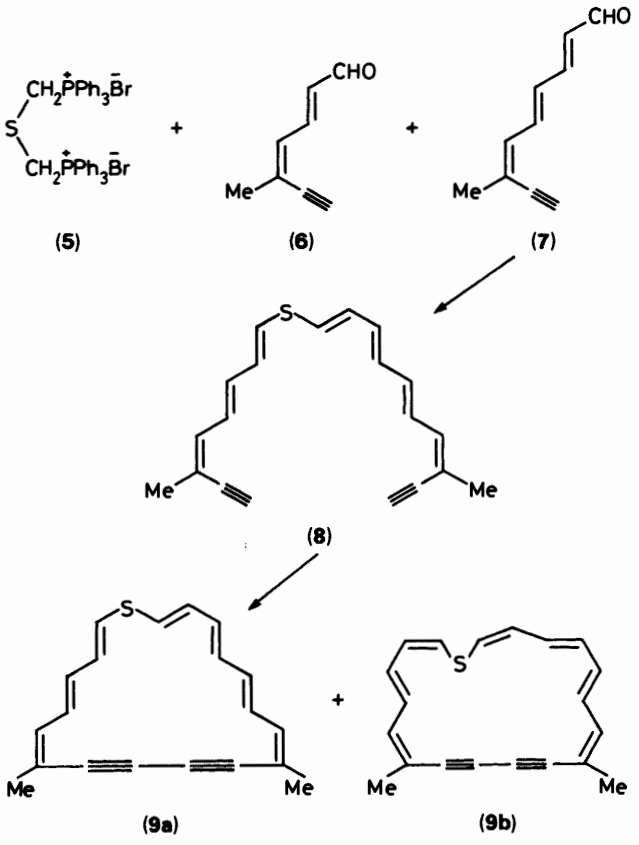
(**4**)

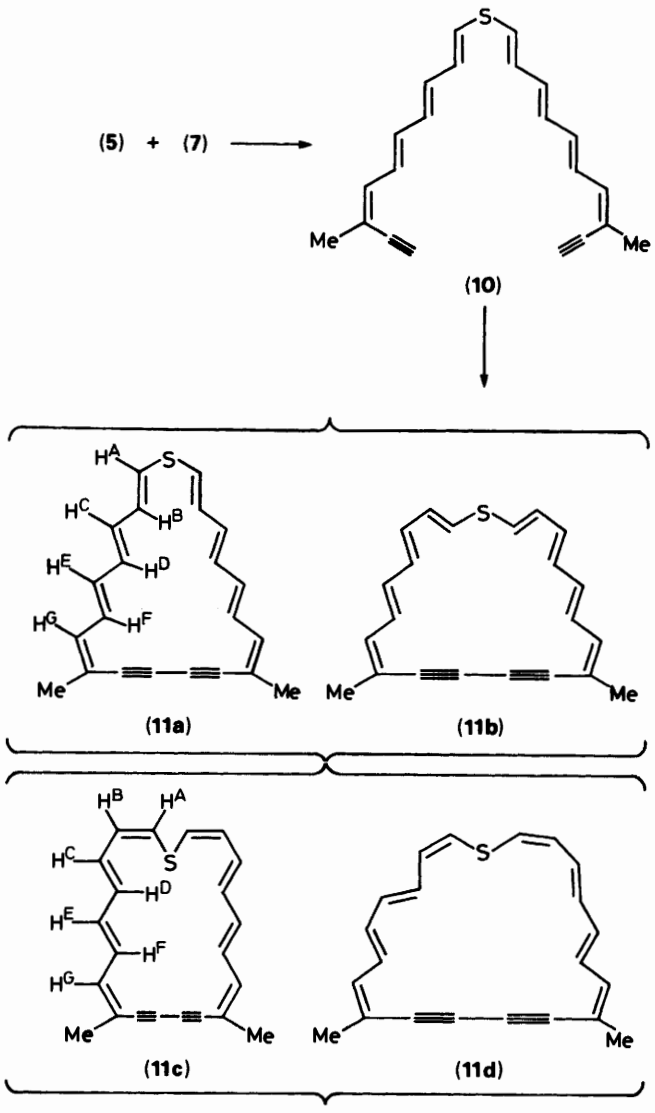
Results and Discussion

Synthesis.—Sondheimer and co-workers have reported a simple general approach to tetradehydro-thia[13]- (**2**),[6] -thia[15]- (**4**),[8] and -thia[17]-annulene (**3**),[7] in which a sulphur atom is flanked by ethylenic bonds on both sides. The method employs a Wittig condensation of the salt, bis[(triphenylphosphonio)methyl] sulphide dibromide (**5**),[10] with appropriate aldehydes containing a terminal acetylene group, followed by an intramolecular oxidative coupling of the resulting acyclic sulphide.

We have now successfully applied the method to the synthesis of higher homologues of (**2**)–(**4**) using the dienyne, trienyne, and tetraenyne aldehydes, which are now relatively readily available,[5,11] as the starting materials, using essentially same approach.[6–8]

Treatment of the salt (**5**)[10] in diethyl ether with 2 molar equiv. of butyl-lithium at room temperature led to the corresponding bis-ylide, which was allowed to react with a mixture of the dienyne aldehyde (**6**)[11] and the trienyne aldehyde (**7**)[11] (1 molar equiv. each) at this temperature. Chromatography of the product on alumina afforded a mixture of stereoisomers of the unsymmetrical acyclic sulphide precursor of the





thia[19]annulene in a 4.1% yield, along with the symmetrical acyclic sulphide precursors of the thia[17]- and thia[21]-annulenes. The 'all-*trans*' isomer (**8**) was isolated from the mixture by recrystallization. Intramolecular oxidative coupling of the mixture containing (**8**) by copper(II) acetate monohydrate in pyridine–methanol at 60 °C under high dilution conditions using diethyl ether as an entraining solvent resulted in a stereoisomeric mixture of the thia[19] annulene (**9**), which was separated into the 'all-*trans*' isomer (**9a**) (1.9%) and the 'di-*cis*' isomer (**9b**) (2.5%) by column chromatography on alumina and then by recycled gel permeation chromatography. Details of the structural and chemical shift assignments are presented later.

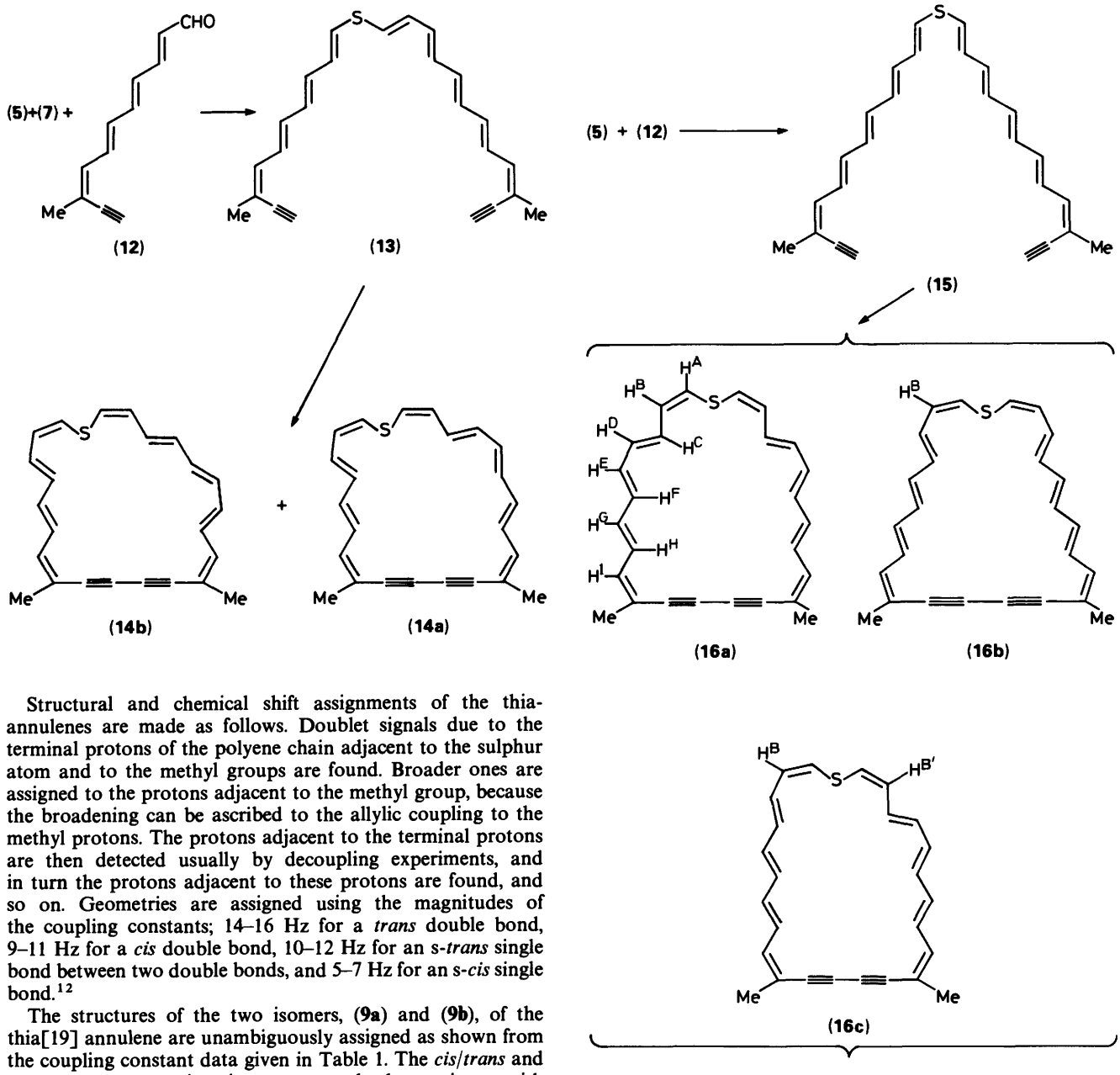
Reaction of (**5**) with BuLi, then with 2 molar equiv. of (**7**) led to steroisomeric acyclic sulphides in an 8.7% yield, from which the 'all-*trans*' isomer (**10**) was isolated. Intramolecular oxidative coupling of the mixture containing (**10**) with anhydrous copper(II) acetate at 50 °C in pyridine–ether under relatively dilute conditions yielded the 'all-*trans*' isomer (**11a**) (2.1%) and the 'di-*cis*' isomer (**11c**) (2.6%) of the thia[21]annulene, separated by chromatography on alumina.

Similarly, reaction of (**5**) with BuLi, then with a mixture of (**7**) and the tetraenyne aldehyde (**12**)[5] (1 molar equiv. each) led to a stereoisomeric mixture of the unsymmetrical sulphide precursors of the thia[23] annulene in 2.9% yield, along with the symmetrical sulphide precursors of the thia[21]- and thia[25]-annulenes. The 'all-*trans*' isomer (**13**) was isolated from the mixture by crystallization. Intramolecular coupling of the mixture containing (**13**) under high dilution conditions, as before, gave the 'di-*cis*' thia[23]annulene (**14**) (1.0%).

Reaction of (**5**) with BuLi, then with 2 molar equiv. of (**12**) gave an isomeric mixture of the symmetrical sulphides in a 4.9% yield, from which the 'all-*trans*' isomer (**15**) was isolated by crystallization. Coupling of the mixture containing (**15**) employing high dilution methods, as before, afforded the 'di-*cis*' thia[25]annulene (**16**) in 2.8% yield.

Although the stereochemistries of all the acyclic sulphides derived from the Wittig condensations were not completely assigned, *trans*-configurations for the newly formed double bonds of the isolated compounds (**8**), (**10**), (**13**), and (**15**) were confirmed both by examination of their IR spectra and, occasionally, by the ^{1}H NMR signals for the acetylenic and methyl protons. All the acyclic sulphides obtained were thermally very unstable and highly sensitive to diffused light and air. These sulphides were stored in solution at low temperature, and were purified by chromatography on alumina immediately prior to oxidative coupling. All the thia-annulenes were also thermally unstable and sensitive to diffused light and air, but were more stable than the corresponding acyclic sulphides. Thus, satisfactory elemental analyses were obtained for compounds (**9a**) and (**11c**).

^{1}H *NMR Spectra*.—The ^{1}H NMR spectra of the thia-annulenes (**9a**), (**9b**), and (**11a**) are presented in Figure 1, and the spectra of (**11c**), (**14**), and (**16**) are shown in Figures 2, 3, and 4, respectively. The chemical shift data are listed in Table 1, together with those of the corresponding acyclic sulphides (**8**), (**10**), (**13**), and (**15**).



Structural and chemical shift assignments of the thia-annulenes are made as follows. Doublet signals due to the terminal protons of the polyene chain adjacent to the sulphur atom and to the methyl groups are found. Broader ones are assigned to the protons adjacent to the methyl group, because the broadening can be ascribed to the allylic coupling to the methyl protons. The protons adjacent to the terminal protons are then detected usually by decoupling experiments, and in turn the protons adjacent to these protons are found, and so on. Geometries are assigned using the magnitudes of the coupling constants; 14–16 Hz for a *trans* double bond, 9–11 Hz for a *cis* double bond, 10–12 Hz for an s-*trans* single bond between two double bonds, and 5–7 Hz for an s-*cis* single bond.[12]

The structures of the two isomers, (**9a**) and (**9b**), of the thia[19] annulene are unambiguously assigned as shown from the coupling constant data given in Table 1. The *cis*/*trans* and s-*cis*/s-*trans* geometries given are completely consistent with the above-mentioned criteria of the coupling constants. ^{1}H NMR spectra of (**9a**) and (**9b**) were also measured at −70 °C (Table 2). On lowering of the temperature, the inner protons move downfield although the outer protons show no clear shifts. The downfield shifts of the inner proton signals may reflect the reduced flexibility of the macrocycle at lower temperatures.

The structures of the 'di-*trans*' isomer (**11a**) of the thia[21]annulene is uniquely assigned as shown, except for the $=CH^B-CH^C=$ single bond; the observed value of J_{BC} is 9 Hz which is somewhat smaller than the 'standard' value for the s-*trans* bond (10–12 Hz). This suggests that the $-CH^A=CH^B-$ double bond is mobile and the compound exists in rapid equilibrium between (**11a**) and the several other conformers such as (**11b**), with (**11a**) as the most abundant conformer. The fact that the outer H^A proton of the diatropic (**11a**) resonates at a relatively high field (Tables 1 and 2) might be reasonable if the minor conformers contribute to some extent. The interconversion among the conformers is still rapid on the NMR time scale even at −100 °C because neither splitting nor broadening of the signals is observed at this temperature (Table 2). Upon lowering of the temperature, H^G, H^E, and H^C move slightly downfield but H^A goes upfield, while H^D and H^F shift upfield and H^B downfield. The behaviour of H^A and H^B proton signals may reflect the mobility of the $-CH^A=CH^B-$ double bond.

The ^{1}H NMR spectrum of the 'di-*cis*' isomer of the thia[21]annulene at 27 °C is shown at the top of Figure 2. From the coupling constants, the *cis*/*trans* configurations of the double bonds are easily fixed. The value of *ca.* 9 Hz for J_{BC} and J_{DE}, intermediate between the standard s-*cis* and s-*trans* values, suggests that the flipping of the $-CH^C=CH^D-$ moiety occurs rapidly at this temperature. The spectrum at −95 °C indicates the presence of *ca.* 40% of a symmetrical conformer (**11c**) and *ca.* 60% of an unsymmetrical conformer, to which structure (**11d**) is assigned. The presence of these conformers was supported by the three methyl proton signals at δ 2.26, 2.22, and 2.10 in 3:4:3 ratio.

Table 1. ^{1}H NMR data of the compounds **(8)**, **(9a)**, **(9b)**, **(10)**, **(11a)**, **(11c)**, **(13)**, **(14)**, **(15)**, and **(16)** in $CDCl_3$ at room temperature.[a]

Compound	Chemical shift/ ppm (Coupling constant/Hz)																	
	H^A	$H^{A'}$	H^B	$H^{B'}$	H^C	$H^{C'}$	H^D	$H^{D'}$	H^E	$H^{E'}$	H^F	$H^{F'}$	H^G	$H^{G'}$	H^H	$H^{H'}$	H^I	$H^{I'}$	Me
(8)[b]	6.77													6.15m					1.95s
(9a)	6.04d	8.09d	7.91dd	6.25dd	5.83dd	6.21dd	8.48dd	7.88dd	6.07br d	5.86dd		8.74dd		6.13br d					1.71s, 1.69s
	(14.5)	(14.5)	(14.5, 11)	(14.5, 6.5)	(15, 11)	(15, 6.5)	(15, 11.5)	(15, 11)	(11.5)	(15, 11)		(15, 11.5)		(11.5)					
(9b)	5.98d	5.67d	5.59dd	5.86dd	5.79dd	8.76dd	8.57dd	5.71dd	5.97br d	5.76dd		9.07dd		6.12br d					1.78s, 1.74s
	(11)	(9)	(11, 7.5)	(11, 9)	(16, 7.5)	(15, 11)	(16, 11)	(15, 6.5)	(11)	(15, 6.5)		(15, 11)		(11)					
(10)[b]	6.77												6.10m						1.96s
(11a)	5.87d		5.54dd		6.73dd		4.93dd		6.91dd		5.27dd		7.02br d						2.18s
	(15)		(15, 9)		(15, 9)		(15, 11)		(15, 11)		(15, 12)		(12)						
(11c)	6.73d		6.49t		6.18dd		5.99dd		6.70dd		5.69dd		6.88br d						2.18s
	(9.5)		(9.5)		(16, 9.5)		(16, 8.5)		(15, 8.5)		(15, 11.5)		(11.5)						
(13)[b]	6.8																	6.1m	1.96s
(14)	6.03d	5.79d	5.68dd	5.93dd	6.01dd	8.04dd	7.51dd	5.87dd	5.96dd	6.45br dd	7.95dd	7.41dd	6.11br d	5.96dd		8.17dd		6.18br d	1.82s, 1.81s
	(11)	(9)	(11, 8)	(11, 9)	(16, 8)	(15, 11)	(16, 10)	(15, 8)	(15, 10)	(15, 8)	(15, 11.5)	(15, 10)	(11.5)	(15, 10)		(15, 11.5)		(11.5)	
(15)[b]	6.8																6.1m		1.95s
(16)	6.53d		6.41t		6.23dd		6.26dd		6.51dd		6.06dd		6.72dd		6.03dd		6.75br d		2.13s
	(9.5)		(9.5)		(15, 9.5)		(15, 7)		(15, 7)		(15, 11)		(15, 11)		(15, 11.5)		(11.5)		

[a] Measured at 500 MHz unless otherwise stated. [b] Measured at 270 MHz. Olefinic protons are not separately identified. Signals due to acetylenic protons are omitted. (See Experimental section.)

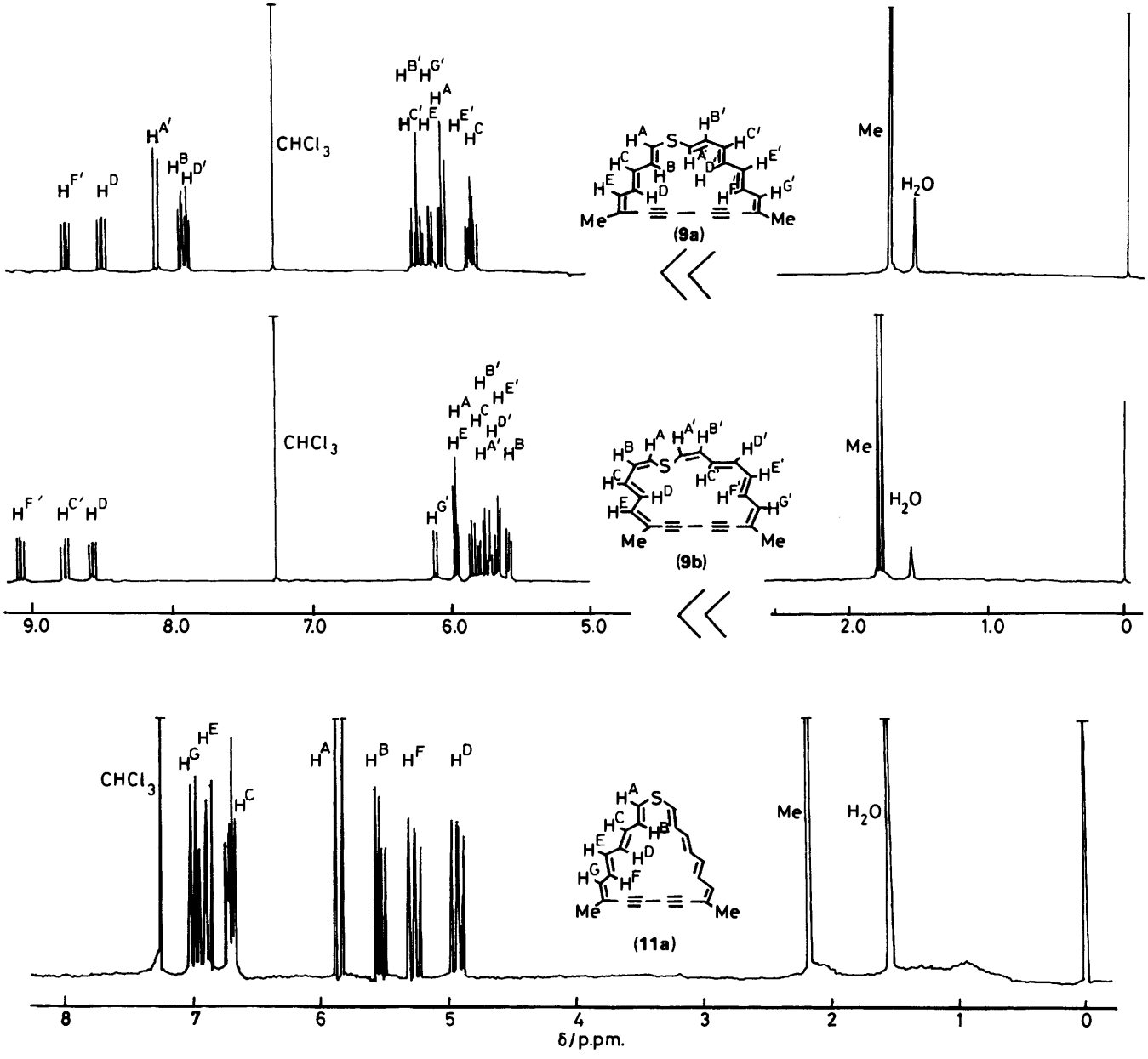


Figure 1. ^{1}H NMR spectra of 'all-*trans*' thia[19]- (**9a**) (500 MHz), 'di-*cis*' thia[19]- (**9b**) (500 MHz), and 'all-*trans*' thia[21]-annulene (**11a**) (270 MHz) in $CDCl_3$ at room temperature.

Table 2. Variable-temperature ^{1}H NMR chemical shifts for the thia-annulenes (**9a**), (**9b**), and (**11a**).

Compound	Temp. (°C)	$H^{F'}$	H^{D}	$H^{A'}$	H^{B}	$H^{D'}$	$H^{B'}$	$H^{C'}$	$H^{G'}$	H^{E}	H^{A}	$H^{E'}$	H^{C}	Me
(**9a**)[a]	27	8.74	8.48	8.09	7.91	7.88	6.25	6.21	6.13	6.07	6.04	5.86	5.83	1.71, 1.69
	−70	8.92	8.64	8.27	8.13	8.04	6.26	6.16	6.14	6.09	6.06	5.88	5.85	1.71, 1.68
		$H^{F'}$	$H^{C'}$	H^{D}	$H^{G'}$	H^{A}	H^{E}	$H^{B'}$	H^{C}	$H^{E'}$	$H^{D'}$	$H^{A'}$	H^{B}	Me
(**9b**)[a]	27	9.07	8.76	8.57	6.12	5.98	5.97	5.86	5.79	5.76	5.71	5.67	5.59	1.78, 1.74
	−70	9.29	8.98	8.76	6.10	6.02	5.99	5.87	5.78	5.77	5.71	5.68	5.59	1.76, 1.74
		H^{G}	H^{E}	H^{C}	H^{A}	H^{B}	H^{F}	H^{D}	Me					
(**11a**)[a]	20	7.05	6.96	6.75	5.88	5.56	5.27	4.96	2.17					
	0	7.08	6.98	6.78	5.87	5.54	5.22	4.92	2.18					
	−40	7.13	7.04	6.83	5.85	5.52	5.22	4.92	2.21					
	−70	7.17	7.09	6.87	5.83	5.51	5.10	4.81	2.23					
	−100	7.22	7.13	6.91	5.82	5.51	5.05	4.77	2.25					

[a] In $CDCl_3$ at 500 MHz. [b] In CD_2Cl_2 at 270 MHz.

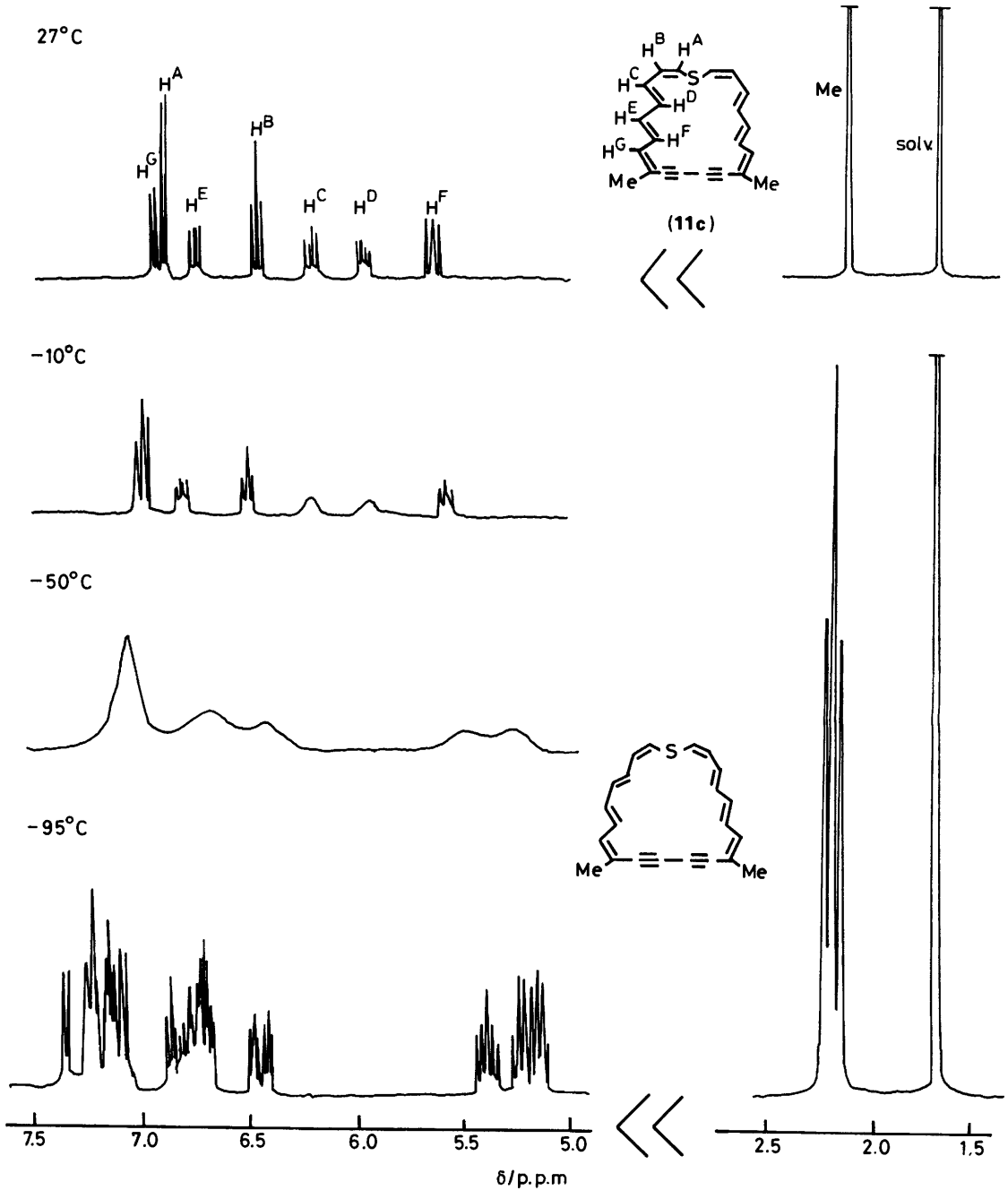


Figure 2. 500 MHz Variable-temperature ^{1}H NMR spectra of 'di-*cis*' thia[21]annulene (**11c**) in [$^2H_8$]-THF.

The spectra of the thia[23]annulene (**14**) are also temperature dependent (Figure 3). The room temperature spectrum is almost consistent with the structure (**14a**) except for the broadening of the $H^{E'}$ and $H^{F'}$ signals, which indicates rapid interconversion among two or more conformers, with (**14a**) the most abundant. The spectrum at −105 °C shows explicitly the presence of *ca.* 80% of (**14a**) and *ca.* 20% of the second conformer. Structure (**14b**), formed by flipping of the $-CH^{E'}=CH^{F'}-$ double bond, is assigned to the minor conformer by detailed examination of the spectrum. The presence of two conformers is not confirmed by the methyl proton signals, since these are obscured by the solvent ([$^2H_8$]-THF) peak.

The spectra of the thia[25]annulene (**16**) are again temperature dependent (Figure 4). The spectrum at 27 °C indicates that the –CH=CH– moiety adjacent to the sulphur atom is *cis* and all the other –CH=CH– moieties are *trans*. The coupling constant J_{BC} is 9.4 Hz which is somewhat smaller than the standard s-*trans* value and J_{DE} is 7.2 Hz which is slightly larger than the standard s-*cis* value. This suggests that the 'average' structure is represented by (**16a**). The frozen spectrum obtained at −95 °C (Figure 4, bottom) is too complex to analyze but suggests the presence of three conformers. Particularly, three signals are found at δ 6.30 (dd, *J* 7 and 9 Hz), δ 6.36 (dd, *J* 7 and 10 Hz), and δ 6.70 (app t, *J* 10.5 Hz) in an intensity ratio of *ca.* 5:3:7. These signals should be assigned to the outer H^B and/or $H^{B'}$ protons of different conformers because they have coupling constants characteristic of a *cis* double bond. The first two have s-*cis* couplings and the last has an s-*trans* coupling. We tentatively consider three conformers (**16a**, **b**, **c**) which are formed by flipping of the $-CH^C=CH^D-$ and $-CH^E=CH^F-$ double bonds, existing in a ratio of *ca.* 7:3:10 (*i.e.* 35%:15%:50%). The signal at δ 6.70 is assigned to the H^B

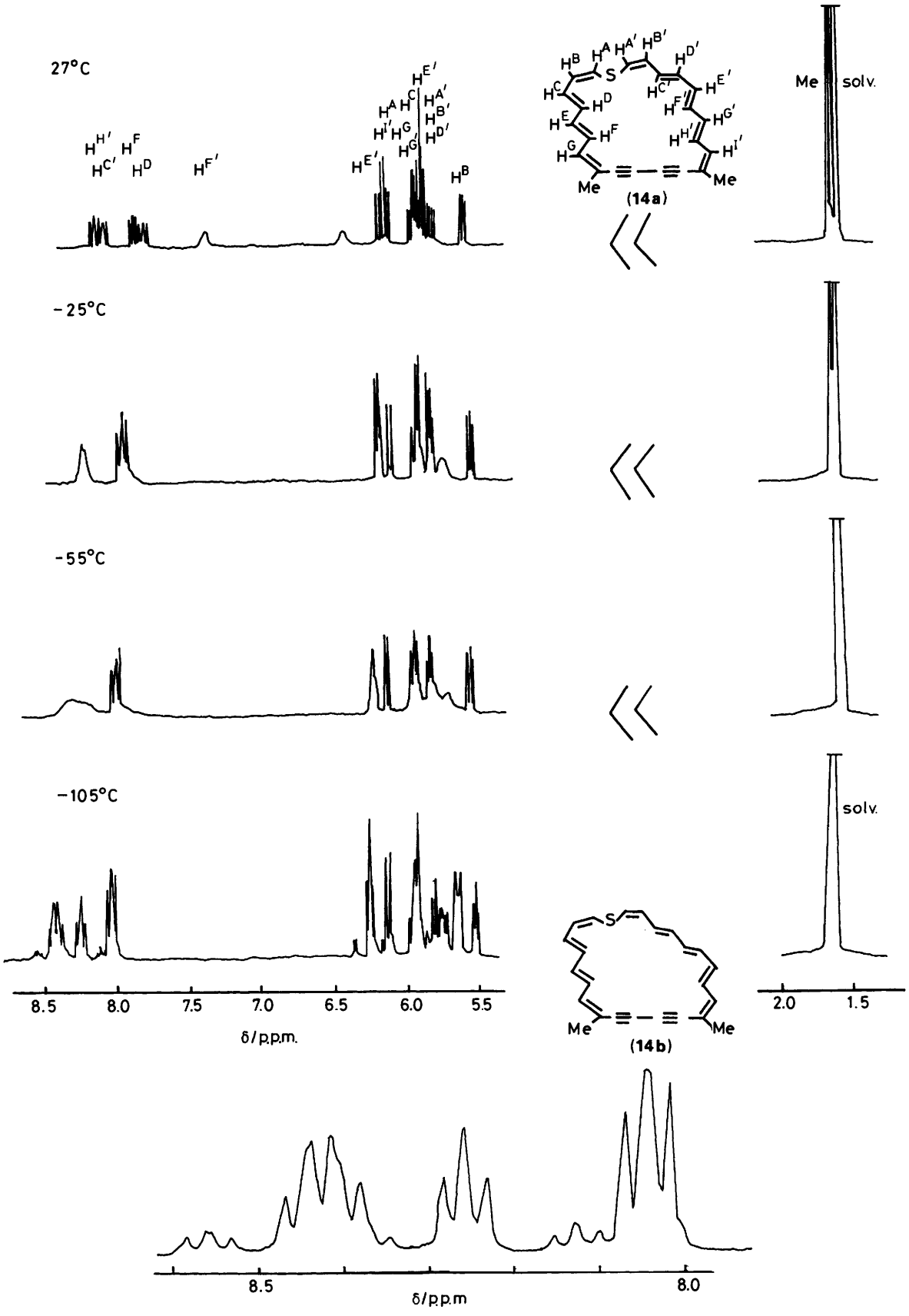


Figure 3. 500 MHz Variable-temperature ^1H NMR spectra of thia[23]annulene (**14**) in [$^2H_8$]-THF. Expanded spectrum of the inner olefinic proton region at −105 °C (bottom).

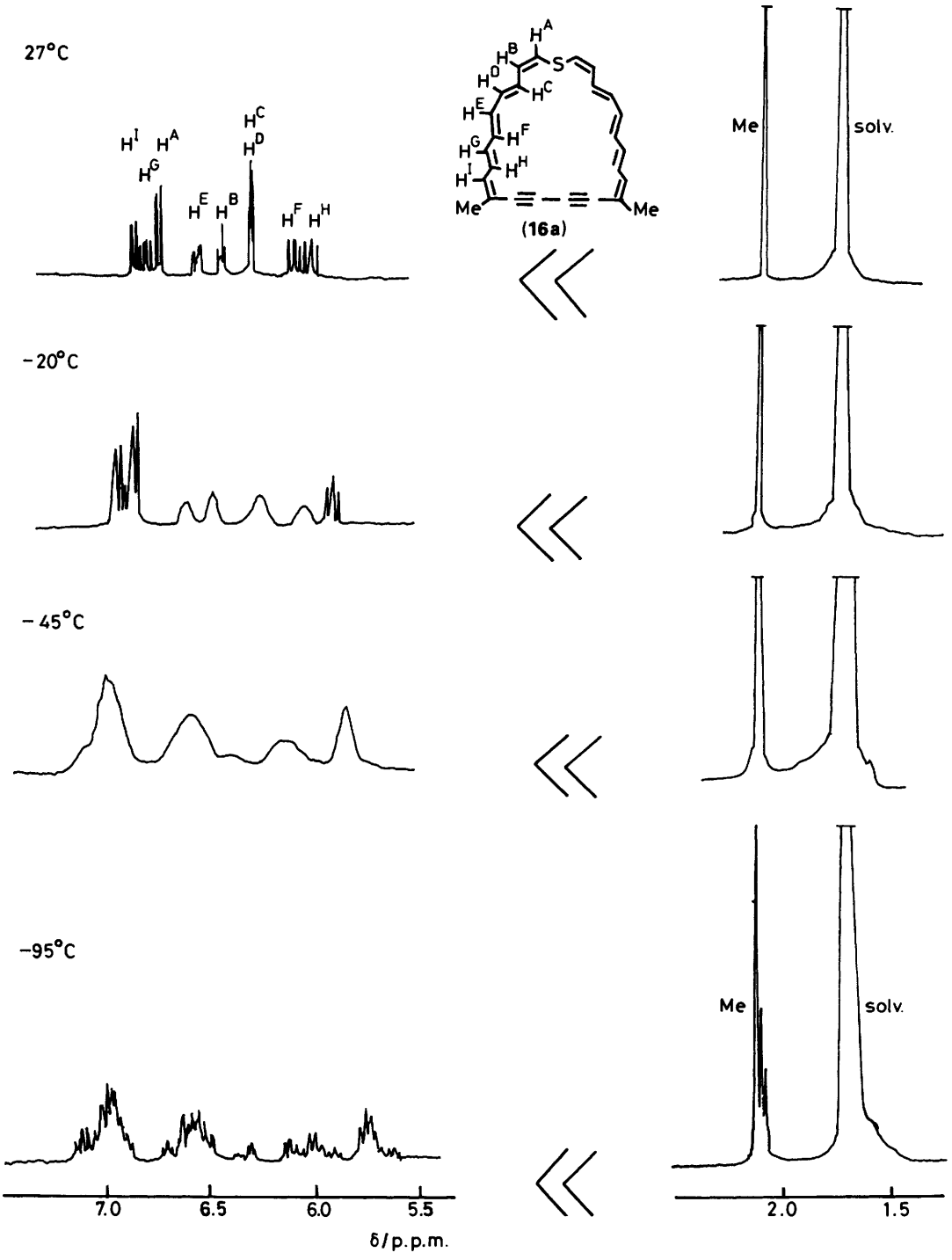


Figure 4. 500 MHz Variable-temperature ^1H NMR spectra of thia[25]annulene (**16**) in [$^2H_8$]-THF.

proton of (**16a**), that at δ 6.36 to the H^B of (**16b**), and that at δ 6.30 to H^B of (**16c**). The signal due to the $H^{B'}$ proton of (**16c**) is not identified because of overlapping with other signals. The methyl proton signals appear as three singlets at δ 2.18, 2.14, and 2.12 in a ratio of 12:5:3. This is understood by considering that (**16a**) gives a singlet at δ 2.18, (**16b**) a singlet at δ 2.12, and (**16c**) two singlets at δ 2.18 and 2.14.

From Table 1, comparison of the ^1H NMR chemical shifts of the various protons of tetradehydrothia[19]annulenes (**9a**, **b**) and tetradehydrothia[23]annulene (**14**) with those of the corresponding acyclic sulphides (**8**) and (**13**) indicates that (**9a**), (**9b**), and (**14**) are paratropic, as might be expected for 20π- and 24π-electron systems, respectively, as has been observed for the 16π-electron system (**4**).[8] This follows from the fact that essentially all the outer protons (including the methyl protons) in (**9a**), (**9b**), and (**14**) resonate at higher field than the corresponding protons in (**8**) and (**13**), respectively, whereas the inner protons in (**9a**), (**9b**), and (**14**) resonate at lower field. Conversely, comparison of the chemical shifts of the protons of (**11a**) with those of the corresponding acyclic model (**10**) indicates that (**11a**) is diatropic, as might be expected for 22π-electron system, and as has been observed for the 14π- (**2**)[6] and

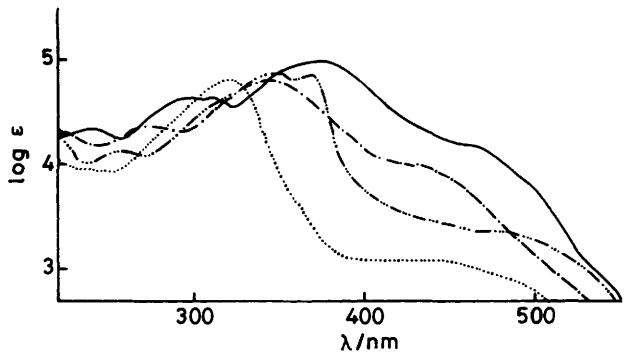


Figure 5. Electronic absorption spectra of thia[19]- (**9a**) (-----), thia[21]- (**11a**) (——-—-), thia[23]- (**14**) (——-—), and thia[25]-annulene (**16**) (——) in THF.

18π-electron system (**3**).[7] This follows from the fact that essentially all the olefinic inner protons in (**11a**) resonate at higher field than the corresponding protons in (**10**), whereas all the outer protons (including the methyl protons) resonate at lower field. The 'di-*cis*' thia[21]- (**11c**) and thia[25]-annulene (**16**) also appeared to be diatropic, as might be expected for 22π- and 26π-electron systems, respectively, since the methyl protons in (**11c**) and (**16**) resonate at lower field than those of (**10**) and (**15**). This was not clearly evident from the olefinic proton shifts, but it becomes clear when it is realized that the spectra of both (**11c**) and (**16**) are temperature-dependent (see above).

It is evident that in the spectra of (**9a**), (**9b**), and (**14**) (Figures 1 and 3) the outer protons resonate at higher field than the inner protons, while in the spectra of (**11a**) (Figure 1), (**11c**) (Figure 2), and (**16**) (Figure 4) essentially all the outer protons are at lower field than the inner ones. This confirms the indicated conformations for the compounds (**9a**), (**9b**), (**11a**), (**11c**), (**14**), and (**16**), and shows that the above-mentioned alternation of the ring current in these thia-annulenes can be deduced without having to make comparisons with the corresponding acyclic models.

The simplest test for the nature of the ring currents in both the tetradehydrothia-annulene and the tetradehydroannulenone series (**1**), which should have similar geometry and planarity, is provided by the chemical shifts of the methyl protons, since these must always be external and can be readily recognized in both series. The alternation of the methyl proton resonances between the thia[4*n* + 1]annulenes {[13]- (**2**):[6] δ 2.29; [17]- (**3**):[7] δ 2.22; [21]- (**11a**): δ 2.18; [25]- (**16**): δ 2.13} (relatively low field) and the thia[4*n* − 1]annulenes {[15]- (**4**):[8] δ 1.61, 1.57; [19]- (**9a**): δ 1.71, 1.67; [23]- (**14**): δ 1.82, 1.81} (relatively high field) confirms the diatropicity of the former and the paratropicity of the latter. This alternation parallels that between the [4*n* + 1]annulenones {[13]- (**1a**):[4] δ 1.74; [17]- (**1c**):[4] δ 1.77; [21]- (**1e**):[4] δ 1.83; [25]- (**1g**):[5] δ 1.86} and the [4*n* − 1]-annulenones {[15]- (**1b**):[4] δ 2.24, 2.18; [19]- (**1d**):[4] δ 2.21, 2.17; [23]- (**1f**):[5] δ 2.14, 2.09}, albeit being in the reverse trend for the same ring size of annulenones (**1**) and to a lesser extent with an increasing ring size.

Thus, it was found that dia- or para-tropicity for the tetradehydrothia-annulene series is observed up to the 25-membered ring size, as found similarly in the case of the tetradehydroannulenones (**1**).

Electronic Spectra.—The electronic absorption spectra of tetradehydro-thia[19]- (**9a**), -thia[21]- (**11a**), -thia[23]- (**14**), and -thia[25]-annulene (**16**) are given in Figure 5. When compared with the spectra of the thia[21]- (**11a**) and thia[25]-annulene (**16**), the spectra of the thia[19]- (**9a**) and the thia[23]-annulene (**14**) show rather broad absorption curves, as recognized in the spectra of carbocyclic [4*n*]π-annulenes and dehydroannulenes.[1]

The absorption maxima of all the tetradehydrothia-annulenes (**9a**), (**9b**), (**11a**), (**11c**), (**14**), and (**16**), together with the wavelengths of the main absorption maxima of (**2**)–(**4**), are listed in Table 3, from which it can be seen that the main maxima of thia[13]- (**2**), thia[17]- (**3**), and thia[21]-annulene (**11a**) ([4*n* + 2]π-electron systems) are at rather longer wavelengths than those of thia[15]- (**3**) and thia[19]-annulene (**9a**) ([4*n*]π-electron systems). Thus, it is evident that in these tetradehydrothia-annulenes the same alternation in the wavelengths of the main absorption maxima between [4*n* + 2]- and [4*n*]-systems occurs as has been demonstrated for monocyclic annulenes and dehydroannulenes.[13] Unfortunately, since only the 'di-*cis*' isomers were obtained for the thia[23]- and the thia[25]-annulenes, and the absorption curves are rather different between the 'di-*cis*' and 'all-*trans*' isomers [*e.g.* between (**9a**) and (**9b**)], it was not possible to use the main maxima of (**14**) and (**16**) for comparison with regard to the above discussion.

Experimental

M.p.s were determined on a hot-stage apparatus and are uncorrected. IR spectra were taken with a Hitachi 260-50 spectrophotometer as KBr discs and were calibrated against polystyrene; only significant maxima are described. UV spectra were measured in tetrahydrofuran solution and run with a Hitachi 220 A spectrophotometer. Mass spectra were recorded with a JEOL JMS-D 300 spectrometer operating at 75 eV using a direct-inlet system or a JEOL JMS-DX 303 spectrometer equipped with JMA-DA 5000 field-desorption system. ^{1}H NMR spectra were recorded as $CDCl_3$ solutions, unless otherwise stated, with a JEOL GX-270 (270 MHz) or a Bruker AM-500 (500 MHz) spectrometer, tetramethylsilane being used as an internal standard. Assignments were clarified by the use of decoupling experiments where necessary. Merck alumina (activity II–III) and silica gel were used for column chromatography. Gel permeation chromatography was performed on an LC-09 Liquid Chromatograph of Japan Analytical Industry Co., Ltd, using a series of JAIGEL H1 and H2 columns and chloroform as eluant. All the Wittig reactions were carried out under argon. Progress of most reactions was followed by TLC using Merck precoated silica gel. Organic extracts were washed with saturated aqueous sodium chloride and dried over anhydrous sodium sulphate prior to removal of solvent. Solvents were evaporated under water-pump pressure. Ether refers to diethyl ether.

3,17-Dimethyl-9-thianonadeca-3,5,7,10,12,14,16-heptaene-1,18-diyne (**8**).—To a stirred suspension of the salt (**5**)[10] (26.4 g, 35.6 mmol) in dry ether (700 ml) was added dropwise a solution of butyl-lithium (1.50M; 47.4 ml, 71.2 mmol) in hexane by syringe during 30 min at 20 °C under argon. After being stirred for 30 min at 20 °C, the mixture was treated dropwise with a solution of the dienyne aldehyde (**6**)[11] (4.28 g, 35. 6 mmol) and the trienyne aldehyde (**7**)[11] (5.21 g, 35.6 mmol) in dry ether (190 ml) during 45 min at 20 °C, and then the solution was stirred for 1 h at 20 °C. After addition of ethyl acetate (48 ml), the mixture was poured onto water, and the aqueous layer was extracted with benzene. The combined organic layers were washed with brine and dried. The product after removal of solvents was chromatographed on alumina (4.2 × 12.0 cm). The fractions eluted with 1–2% ether in hexane afforded a mixture of acyclic sulphides of the thia[17]annulene (108 mg, 1.1%). The fractions eluted with 3–5% ether in hexane afforded a stereoisomeric mixture of acyclic sulphides of the desired thia[19]annulene (425 mg, 4.1%) as a very unstable semi-solid. Recrystallization of this semi-solid from hexane gave the 'all-

Table 3. Electronic absorption maxima of thia-annulenes (**2**)–(**4**), (**9a**), (**9b**), (**11a**), (**11c**), (**14**), and (**16**) in THF. The strongest absorptions of (**2**)–(**4**), (**9a**), and (**11a**) are indicated in bold type.

	λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1})
[13]-(**2**)	**295**[a]
[15]-(**4**)	**288**[b]
[17]-(**3**)	**322**[c]
[19]-(**9a**)	237sh (9 200), 311sh (56 500), **320** (**62 200**), 462sh (1 060)
(**9b**)	248 (15 300), 320 (57 500), 345 (49 500), 428 (2 670)
[21]-(**11a**)	224 (19 900), 273 (22 600), 283sh (22 000), **345** (**63 500**), 431sh (9 890)
(**11c**)	226 (27 400), 276 (33 700), 291 (28 000), 354 (62 100), 440sh (8 840)
[23]-(**14**)	261 (17 600), 319sh (55 600), 349 (71 200), 369 (73 200), 440sh (6 860)
[25]-(**16**)	230sh (19 900), 244 (21 400), 296 (41 300), 310 (44 400), 374 (93 800), 460sh (16 000)

[a] In diethyl ether, see ref. 6. [b] See ref. 8. [c] See ref. 7.

trans' sulphide (**8**) (325 mg, 3.1%) as yellow needles, m.p. 82–84 °C (decomp.); *m/z* 292.1286 ($C_{20}H_{20}S$ requires *M*, 292.1286); λ_{max} 279sh (ε 25 300 dm^3 mol^{-1} cm^{-1}), 291 (29 500), 311sh (34 000), 324 (36 900), and 389 nm (64 000); ν_{max} 3 270 (C≡CH), 2 080 (C≡C), 1 000, and 990 cm^{-1} (*E* HC=CH); δ(270 MHz) 6.77–6.15 (12 H, m, olefinic H), 3.35 (1 H, s, C≡CH), 3.33 (1 H, s, C≡CH), and 1.95 (6 H, s, Me) (Found: C, 81.3; H, 6.7. $C_{20}H_{20}S$ requires C, 82.1; H, 6.9%). Attempts to improve the elemental analysis failed. The fractions eluted with 7–10% ether in hexane afforded a mixture of acyclic sulphides of the thia[21]annulene (see below) (171 mg, 1.5%). The later fractions eluted with 15% ether in hexane afforded the recovered aldehydes (**6**) and (**7**) (500 mg).

Isomeric 7,12-*Dimethyl*-8,9,10,11-*tetradehydrothia*[19]*annulenes* (**9a**) *and* (**9b**).—A solution of a mixture of compound (**8**) and its stereoisomers (425 mg, 1.45 mmol) in pyridine (64 ml) and dry ether (50 ml) was added dropwise during 4 h to a stirred solution of copper(II) acetate monohydrate (1.70 g) in pyridine (255 ml), dry ether (228 ml), and methanol (85 ml) at 60–62 °C, and then the mixture was stirred for further 30 min at 60 °C. The mixture was then poured onto water and extracted with benezene. The extracts were washed repeatedly with 5% HCl until they turned acidic, and then with aqueous sodium hydrogen carbonate, and dried and concentrated. The residue was chromatographed on alumina (3.2 × 9.3 cm). The fractions eluted with 3–5% ether in hexane afforded a semi-solid containing the desired thia[19]annulene, which was shown to be a *ca.* 3:2 mixture of isomers. The solid was subjected to gel permeation chromatography with chloroform as eluant. After recycling (25 ×), two well-separated bands were observed. The earlier, less abundant band afforded the unstable 'all-*trans*' *thia*[19]*annulene* (**9a**) (8 mg, 1.9%) as orange needles, m.p., 172–174 °C (decomp.) (from hexane); *m/z* 290 (M^+, 92%) and 215 (100); M^+, 290.4; for UV data see Table 3 and Figure 5; ν_{max} 2 150 (C≡C) and 980 cm^{-1} (*E* HC=CH); for ^{1}H NMR data see Tables 1, 2, and Figure 1 (Found: C, 82.4; H, 6.35. $C_{20}H_{18}S$ requires C, 82.7; H, 6.25%). The later band afforded the 'di-*cis*' *thia*[19]*annulene* (**9b**) (10 mg, 2.5%) as orange needles, m.p. 160–163 °C (decomp.); *m/z* 290.1128 ($C_{20}H_{18}S$ requires *M*, 290.1128); for UV data see Table 3: ν_{max} 2 170 (C≡C), 970 (*E* HC=CH), 700, and 680 cm^{-1} (*Z* HC=CH); for ^{1}H NMR data see Tables 1, 2, and Figure 1.

3,19-*Dimethyl*-11-*thiahenicosa*-3,5,7,9,12,14,16,18-*octaene*-1,20-*diyne* (**10**).—To a stirred suspension of the salt (**5**)[10] (1.27 g, 1.71 mmol) in dry ether (33 ml) was added dropwise a solution of BuLi (1.57M; 2.17 ml, 3.42 mmol) in hexane by syringe during 10 min at 20 °C under argon. The mixture was stirred for 30 min at 20 °C, then a solution of the trienyne aldehyde (**7**)[11] (500 mg, 3.42 mmol) in dry ether (11 ml) was added dropwise during 20 min at 20 °C. The mixture was stirred for 5 h at 20 °C, then worked-up as for the isolation of (**8**). The product was chromatographed on alumina (3.2 × 4.9 cm). The initial fractions eluted with 5–7% ether in hexane afforded a mixture of (**10**) and its steroisomers (95 mg, 8.72%) as a semi-solid. Recrystallization of the solid from hexane–benzene afforded the 'all-*trans*' *isomer* (**10**) (73 mg, 6.7%) as very unstable yellow needles, m.p. 84–86 °C (decomp.); *m/z* 318.1478 ($C_{22}H_{22}S$ requires *M*, 318.1442); λ_{max} 317sh (ε 28 900 dm^3 mol^{-1} cm^{-1}), 331 (32 400), 379sh (43 000), and 396 nm (45 700); ν_{max} 3 280 (C≡CH), 2 200 (C≡C), and 990 cm^{-1} (*E* HC=CH); δ(270 MHz) 6.77–6.10 (14 H, m, olefinic H), 3.35 (2 H, s, C≡CH), and 1.96 (6 H, s, Me). The later fractions eluted with 10% ether in hexane afforded the recovered aldehyde (**7**) (105 mg).

Isomeric 9,14-*Dimethyl*-10,11,12,13-*tetradehydrothia*[21]*annulenes* (**11a**) *and* (**11c**).—A solution of compound (**10**) and its stereoisomers (433 mg, 1.36 mmol) in pyridine (75 ml) and dry ether (25 ml) was added dropwise during 4 h to a stirred solution of anhydrous copper(II) acetate (4.94 g) in pyridine (102 ml) and dry ether (36 ml) at 50 °C, and the mixture was stirred for further 1 h at the same temperature. The mixture was worked-up as for the isolation of (**9**), and the product was chromatographed on alumina (3.2 × 8.3 cm). The initial fractions eluted with 5–8% ether in hexane afforded the 'all-*trans*' *thia*[21]*annulene* (**11a**) (9 mg, 2.1%) as red needles, m.p. 182–184 °C (decomp.) (from hexane); *m/z* 316.1304 ($C_{22}H_{20}S$ requires *M*, 316.1322); for UV data see Table 3 and Figure 5; ν_{max} 2 170 (C≡C) and 970 cm^{-1} (*E* HC=CH); for ^{1}H NMR data see Tables 1, 2, and Figure 1 (Found: C, 82.6; H, 6.5. $C_{22}H_{20}S$ requires C, 83.5; H, 6.4%). Attempts to improve the elemental analysis failed. The later fractions eluted with 8% ether in hexane afforded the 'di-*cis*' *thia*[21]*annulene* (**11c**) (11 mg, 2.6%) as orange needles, m.p. 166–168 °C (decomp.) (from hexane); *m/z* 316 (M^+, 100%); *M*, 316.4; for UV data see Table 3; ν_{max} 2 170 (C≡C), 995 (*E* HC=CH), and 680 cm^{-1} (*Z* HC=CH); for ^{1}H NMR data see Table 1 and Figure 2 (Found: C, 83.4; H, 6.5. $C_{22}H_{20}S$ requires C, 83.5; H, 6.4%).

3,21-*Dimethyl*-11-*thiatricosa*-3,5,7,9,12,14,16,18,20-*nonaene*-1,22-*diyne* (**13**).—To a stirred suspension of the salt (**5**)[10] (18.5 g, 24.9 mmol) in dry ether (664 ml) was added dropwise a solution of BuLi (1.50M; 33.2 ml, 49.8 mmol) in hexane by syringe during 10 min at 20 °C under argon. After being stirred for 30 min at 20 °C, a solution of the trienyne aldehyde (**7**)[11] (2.80 g, 19.2 mmol) and the tetraenyne aldehyde (**12**)[5] (3.30 g, 19.2 mmol) in dry ether (166 ml) was added dropwise during 30 min at 20 °C, and the mixture was stirred for 3 h at 20 °C. The mixture was worked up as for the isolation of (**8**), and the

product was chromatographed on alumina (4.2 × 13.8 cm). The initial fractions eluted with 2–5% ether in hexane afforded compound (**10**) and its isomers (219 mg, 3.6%). The following fractions eluted with 5–7% ether in hexane afforded a very unstable, stereoisomeric mixture of acyclic sulphides of the thia[23]annulene (193 mg, 2.92%). Recrystallization from hexane afforded the 'all-*trans*' *isomer* (**13**) (125 mg, 1.9%) as yellow needles, m.p. 79–80 °C (decomp.); *m/z* 344 (M^+) (field desorption method); M^+, 344.5; λ_{max} 303sh (ε 21 300 dm^3 mol^{-1} cm^{-1}), 316 (24 700), 347sh (29 700), and 404 nm (53 600); ν_{max} 3 270 (C≡CH), 2 100 (C≡C), and 1 000 cm^{-1} (*E* HC=CH); δ(270 MHz) *ca.* 6.8–6.1 (16 H, m, olefinic H), 3.35 (2 H, s, C≡CH), and 1.96 (6 H, s, Me). The following fractions eluted with 7–10% ether in hexane afforded the compound (**15**) and its isomers (105 mg, 1.5%). The following fractions eluted with 10–15% ether in hexane afforded the recovered trienyne aldehyde (**7**) (320 mg). The later fractions eluted with 15–20% ether in hexane afforded the recovered tetraenyne aldehyde (**12**) (450 mg).

9,14-*Dimethyl*-10,11,12,13-*tetradehydrothia*[23]*annulene* (**14**).—A solution of compound (**13**) and its isomers (385 mg, 1.18 mmol) in pyridine (60 ml) and dry ether (30 ml) was added dropwise during 4 h to a stirred solution of copper(II) acetate monohydrate (2.31 g) in pyridine (231 ml), dry ether (116 ml), and methanol (39 ml) at 60–62 °C. After being stirred for further 1 h at the same temperature, the mixture was worked up as for the isolation of (**9**). The product was chromatographed on alumina (3.6 × 7.5 cm). The fractions eluted with 3–5% ether in hexane afforded the 'di-*cis*' *thia*[23]*annulene* (**14**) (4.0 mg, 1.0%) as orange needles, m.p. 148–150 °C (decomp.) (from hexane); *m/z* 342.1471 ($C_{24}H_{22}S$ requires *M*, 342.1441); for UV data see Table 3 and Figure 5; ν_{max} 2 160 (C≡C), 990, 965 (*E* HC=CH), and 680 cm^{-1} (*Z* HC=CH); for ^1H NMR data see Table 1 and Figure 3.

3,23-*Dimethyl*-13-*thiapentacosa*-3,5,7,9,11,14,16,18,20,22-*decaene*-1,24-*diyne* (**15**).—To a stirred suspension of the salt (**5**)[10] (8.68 g, 11.7 mmol) in dry ether (234 ml) was added dropwise a solution of BuLi (1.50M; 15.6 ml, 23.4 mmol) in hexane by syringe during 10 min at 20 °C under argon. After being stirred for 30 min, a solution of the tetraenyne aldehyde (**12**)[5] (4.03 g, 23.4 mmol) in dry ether (78 ml) was added dropwise during 30 min at 20 °C, and the mixture was stirred for a further 2 h at 20 °C. Then the mixture was worked up as for the isolation of (**8**). The product was chromatographed on alumina (3.6 × 8.2 cm). The fractions eluted with 5–8% ether in hexane afforded a stereoisomeric mixture of the very unstable, acyclic sulphides of the thia[25]annulene (214 mg, 4.9%). Recrystallization from hexane afforded the *compound* (**15**) (182 mg, 4.19%) as yellow needles, m.p. 90–92 °C (decomp.); *m/z* 370 (M^+) (field desorption method); M^+ 370.5; λ_{max} 317sh (ε 11 500 dm^3 mol^{-1} cm^{-1}), 332sh (13 500), 354 (16 200), 397sh (22 700), and 411 nm (24 200); ν_{max} 3 250 (C≡CH), 2 060 (C≡C), and 995 cm^{-1} (*E* HC=CH); δ(270 MHz) *ca.* 6.8–6.1 (18 H, m, olefinic H), 3.35 (2 H, s, C≡CH), and 1.95 (6 H, s, Me).

11,16-*Dimethyl*-12,13,14,15-*tetradehydrothia*[25]*annulene* (**16**).—A solution of the compound (**15**) and its isomers (214 mg, 0.578 mmol) in pyridine (35 ml) and dry ether (18 ml) was added dropwise during 2.5 h to a stirred solution of copper (II) acetate monohydrate (0.86 g) in pyridine (128 ml), dry ether (104 ml), and methanol (21 ml) at 60 °C, and the mixture was stirred for a further 1 h at the same temperature. The mixture was worked up as for the isolation of (**9**), and the product was chromatographed on alumina (3.2 × 4.3 cm). The fractions eluted with 10% ether in hexane afforded the thia[25]annulene as a semi-solid which was further purified by preparative thin-layer chromatography. The fast moving, first band afforded the 'di-*cis*' *thia*[25]*annulene* (**16**) (6.0 mg, 2.8%) as orange needles, m.p. 147–148 °C (decomp.) (from hexane); *m/z* 368.1598 ($C_{26}H_{24}S$ requires *M*, 368.1598); for UV data see Table 3 and Figure 5; ν_{max} 2 150 (C≡C), 960 (*E* HC=CH), and 670 cm^{-1} (*Z* HC=CH); for ^1H NMR data see Table 1 and Figure 4.

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