

## Synthesis and Properties of Methanothia-[15]-, -[17]-, -[19]-, -[21]-, -[23]-, -[25]-, -[27]-, -[29]-annulene and Dimethanodithia-[26]- and -[30]-annulene

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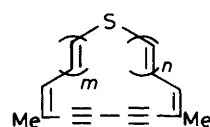
Double Wittig reactions of the vinylogues of cyclohepta-1,3,5-triene-1,6-dicarbaldehyde with bis[(triphenylphosphonio)methyl] sulphide dibromide afforded the corresponding monomeric and/or dimeric condensation products, *i.e.* singly methano-bridged thia-annulenes and/or doubly methano-bridged dithia-annulenes; their  $^1\text{H}$  NMR spectra showed that the methanothia-[17]-, -[19]-, -[23]-, and -[27]-annulene sustain ring current, while the methanothia-[15]-, -[21]-, -[25]-, and -[29]-annulene as well as the dimethanodithia-[26]- and -[30]-annulene do not. Dynamic NMR analysis of the methylene protons revealed the flipping of the methylene bridge above and below the average plane of the macrocycle.

A variety of heteroannulenes have so far been prepared.<sup>1</sup> In the thia-annulene series, the known examples of large rings to show ring-current effect are the tetrahydrothia-[13]- (1;  $m = n = 1$ ), -[15]- (1;  $m = 1, n = 2$ ), and -[17]-annulene (1;  $m = n = 2$ ) as well as their cyclohexene annelated derivatives, prepared by Sondheimer and co-workers.<sup>2</sup> The methano-bridged thia-[11]annulene (2a) and oxa[11]annulene (2b) have also been prepared by a double Wittig reaction between 1,6-diformylcycloheptatriene (3a)<sup>3</sup> and bis[(triphenylphosphonio)methyl] sulphide dibromide (4a),<sup>4</sup> and bis[(triphenylphosphonio)methyl] ether dibromide (4b),<sup>5</sup> respectively, and both products (2a) and (2b) have been shown to be atropic, due to severe deviation of the annulene perimeter from planarity, by Vogel *et al.*<sup>6</sup> This, and the availability of a series of vinylogous dicarbaldehydes (3b)–(3j), prepared by successive homologation from (3a) in connection with our studies of tetrahydromethanoannulenes<sup>7</sup> and methanoannulenes,<sup>8</sup> prompted us to attempt the synthesis of the higher homologues of (2a) or (2b), and to determine the limiting ring size showing a ring current effect in these methanoheteroannulene series. Since a methano-bridge should contribute to keeping the annulene perimeter planar,<sup>9</sup> it was expected that thia- or oxa-annulenes larger than those known, *e.g.* (1;  $m = n = 2$ ),<sup>2</sup> would show the ring-current effect. In fact, the methanothia-[23]- (11) and -[27]-annulene (13) proved to be paratropic; these are the largest heteroannulenes to show the ring-current effect and to be obtained so far.<sup>1</sup>

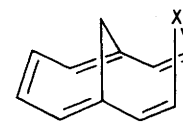
The methylene protons of the methanothia-annulenes prepared in this study give either an AB-quartet or a singlet at room temperature, depending on the compound. The appearance reflects the height of the energy barrier for flipping of the methylene bridge above and below the average plane of the macrocycle. Dynamic NMR analyses were performed for some of the compounds to obtain the energy barrier for the methylene flipping, which would be related to the rigidity of the macrocycle.

### Results and Discussion

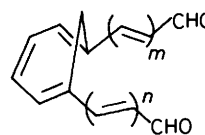
**Synthesis.**—Successive homologations of the dicarbaldehyde (3a) to the vinylogous dicarbaldehydes (3b)–(3j) were carried out by Wittig reactions with a 1.3 or an 8.0 molar equiv. excess of [(1,3-dioxolan-2-yl)methyl]triphenylphosphonium bromide



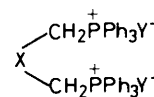
(1)  $m = 1 \sim 2$   
 $n = 1 \sim 2$



(2a)  $X = \text{S}$   
(2b)  $X = \text{O}$

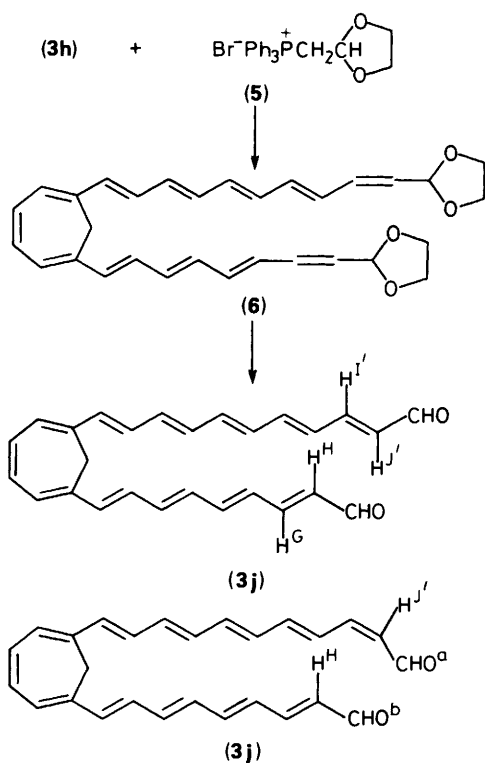


(3a)  $m = n = 0$   
(3b)  $m = 1, n = 0$   
(3c)  $m = n = 1$   
(3d)  $m = 2, n = 1$   
(3e)  $m = n = 2$   
(3f)  $m = 3, n = 2$   
(3g)  $m = n = 3$   
(3h)  $m = 4, n = 3$   
(3i)  $m = n = 4$   
(3j)  $m = 5, n = 4$



(4a)  $X = \text{S}, Y = \text{Br}$   
(4b)  $X = \text{O}, Y = \text{Br}$   
(4c)  $X = \text{O}, Y = \text{Cl}$

(5),<sup>10</sup> followed by immediate hydrolysis, according to the previously reported method.<sup>7,8</sup> However, large quantities of the dicarbaldehydes (3b)–(3j) were required in this study, since the yields of the desired methanothia-annulenes from the reactions between the salt (4a) and the dialdehydes (3b)–(3j) were poor. An improved procedure for the preparation of dialdehydes (3b)–(3j) was therefore developed. The Wittig condensation products, *i.e.* the monoacetal of (3b) or the bisacetal of (3c)–(3j), *e.g.* (6) (see below), were purified by chromatography over alumina before hydrolysis. Hydrolysis of these purified acetals was then

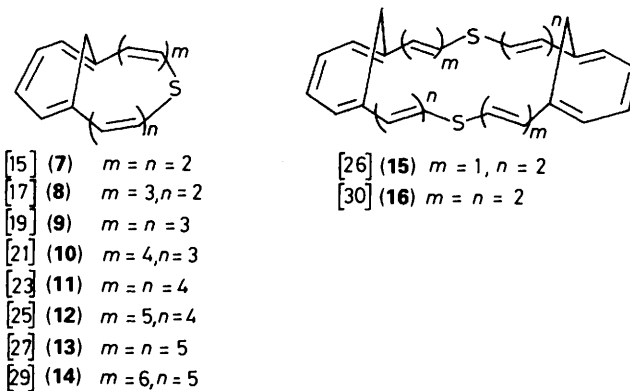


Scheme 1.

carried out with dil. hydrochloric acid in ethanol, admixed with tetrahydrofuran (THF) when the acetal had low solubility in ethanol. With these modifications, compounds (3b)–(3j) were prepared more readily and in higher yields (by 10–20%) than those prepared by employing the previously described method, but the homologated double bonds adjacent to the formyl groups occasionally had the *Z*-configuration, as exemplified in the preparation of the dicarbaldehyde (3j) in Scheme 1.

As modelled in the preparation of the methanothia[11]annulene (2a),<sup>6</sup> a double Wittig reaction between 1,6-bis-(2-formylvinyl)cyclohepta-1,3,5-triene (3c) and the salt (4a) with lithium ethoxide in *N,N*-dimethylformamide (DMF) at 80 °C afforded a monomeric condensation product, 6,11-methanothia[15]annulene (7) (5.2%) as well as the corresponding dimeric product, 6,11:21,26-dimethano-1,16-dithia[30]annulene (16) (10.4%). The reactions between the dialdehyde (3c) and bis[(triphenylphosphonio)methyl] ether dichloride (4c)<sup>11</sup> with butyl-lithium in THF at –60 °C or with ethanolic lithium ethoxide in DMF at 70 °C did not afford the desired methano[15]- and dimethanodioxo[30]-annulene; similarly, attempted preparations of the higher homologues of monocyclic tetrahydrooxa[13]annulene<sup>2</sup> or its dibenzannelated derivative<sup>11</sup> were unsuccessful. Reaction of 1-formyl-6-(2-formylvinyl)cyclohepta-1,3,5-triene (3b) and the salt (4a) afforded only a dimer, 4,9:17,22-bismethano-1,14-dithia[26]annulene (15) in 2.7% yield. The reactions of the higher dicarbaldehydes (3d)–(3j) with the salt (4a) afforded the corresponding monomeric condensation products, 6,11-methanothia[17]- (8) (1.6%), 8,13-methanothia[19]- (9) (1.4%), 8,13-methanothia[21]- (10) (3.8%), 10,15-methanothia[23]- (11) (6.5%), 10,15-methanothia[25]- (12) (1.5%), 12,17-methanothia[27]- (13) (5.2%), and 12,17-methanothia[29]-annulene (14) (4.1%), respectively.<sup>12</sup> These methanothia-annulenes (7)–(14) as well as the dimethanodithia-annulenes (15) and (16) gave satisfactory elemental analyses except for the thia-[21]- (10) and -[29]-annulene (14), and they were obtained as coloured crystals and proved to be thermally

unstable and sensitive to diffused light and air; in particular, compound (14) rapidly decomposed even after recrystallization from common organic solvents at low temperature.



However, of the methanothia-annulenes thus obtained, the thia-annulenes (11)–(14) with a larger than 23-membered ring were shown to be a mixture of two or more stereoisomers from examination of their <sup>1</sup>H NMR spectra (see below), and the isomers could not be separated by preparative TLC or recycled gel permeation chromatography.

In the formation of the methanothia-[19]- (9) and -[23]-annulene (11) [and also, probably, of annulenes (10) and (12)–(14)], a configurational change of the double bond occurred during the Wittig condensations (see below). A similar change has been observed in the preparations of tetrahydro[15]-annulene<sup>13</sup> and tetrahydrotribenzo[14]annulene.<sup>14</sup>

**Structural Analysis.**—The general procedure to assign the geometry and chemical shifts of the polyene moieties connecting a sulphur atom and cycloheptatriene ring of the methanothia-annulenes (7)–(14) was as follows. Doublet signals due to the terminal protons of the polyene chain were found. Then the protons adjacent to the terminal protons were determined usually by the aid of decoupling experiments, and in turn the protons adjacent to these protons were found, and so on. Geometries were assigned using the magnitude of the coupling constants: 14–16 Hz for a *E*-double bond, 9–11 Hz for a *Z*-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.<sup>15</sup>

The <sup>1</sup>H NMR spectra of compounds (7)–(10) and (14) taken at room temperature are shown in Figure 1, and the spectra of compounds (11)–(13) at various temperatures are given in Figures 2–5. The chemical shifts and the coupling constants are given in the Experimental section.

The coupling pattern in the spectrum of 6,11-methanothia[15]annulene (7) indicates that the diene moieties connecting the sulphur atom and the cycloheptatriene ring have a *Z, E* geometry with an *s-trans* conformation for the single bond between the two double bonds. Two possibilities for the structural assignment are therefore available and the structure (7A) with a *Z*-double bond adjacent to the sulphur atom is more likely from an inspection of Dreiding models. As seen from Figure 1, the olefinic protons resonate at almost the same field, suggesting that the thia[15]annulene (7A) is atropic. This may reflect the poor planarity of the 15-membered ring. Inspection of the Dreiding models shows, however, that the molecule is considerably folded. Also, the methylene protons of (7A) give an AB-quartet signal, and the low-field doublet is broadened due to long-range couplings with the H<sup>a</sup> and H<sup>b</sup> protons and this enabled us to assign the doublet to the proton H<sup>b</sup> *anti* to the cycloheptatriene moiety. As regards the position of the bridge protons with respect to the annulene ring of (7A) (and also, of

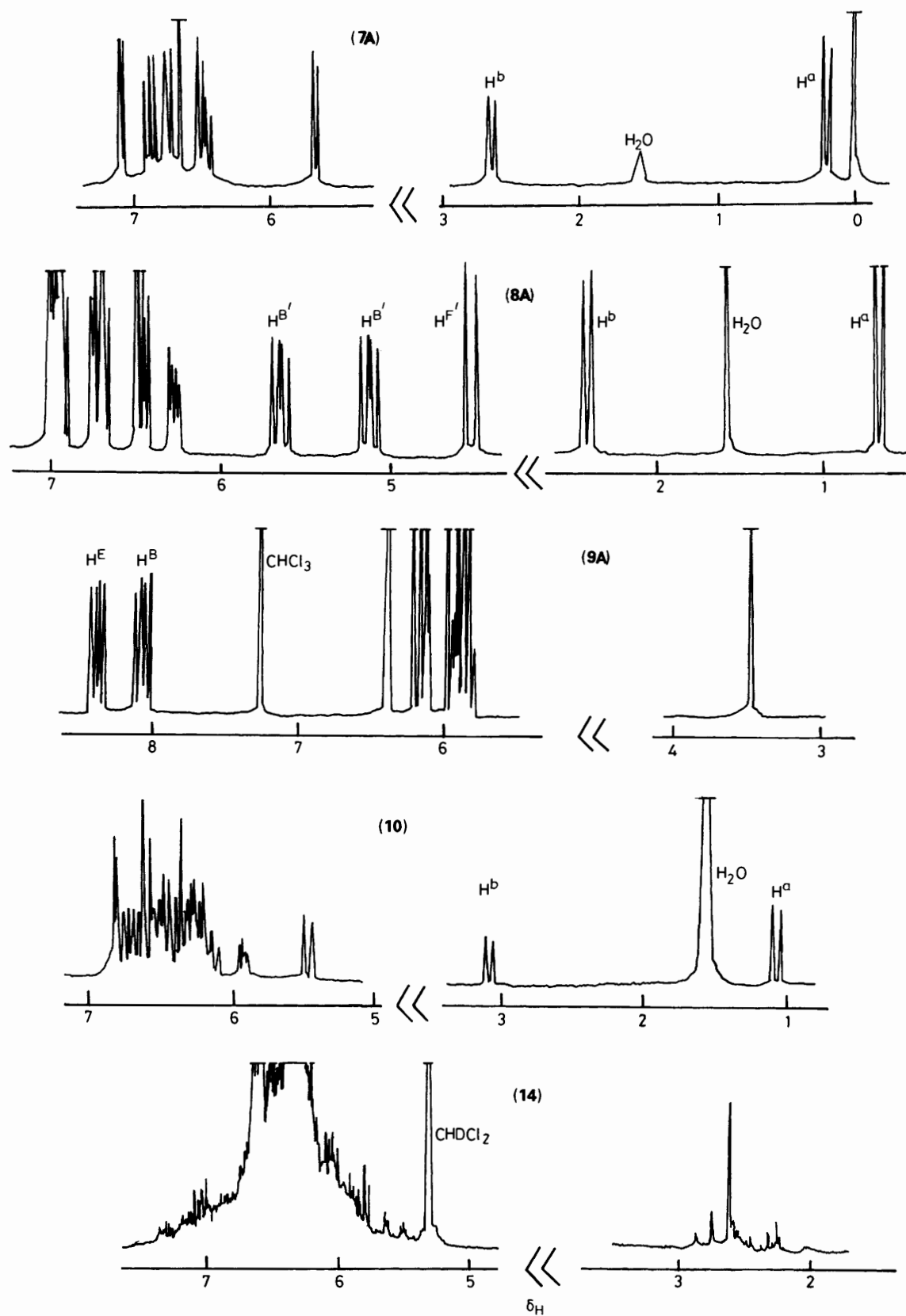
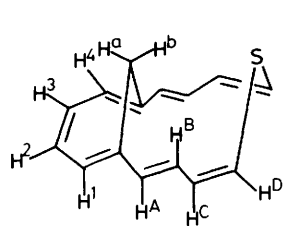
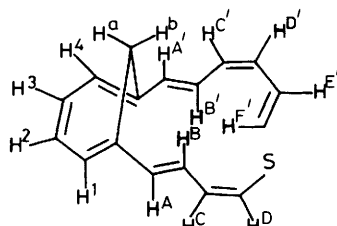


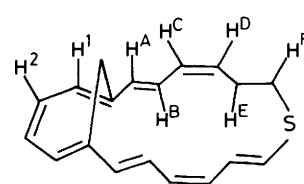
Figure 1. 270 MHz  $^1\text{H}$  NMR spectra of thia[15]- (7A), -[17]- (8A), -[19]- (9A), -[21]-annulene (10) (in  $\text{CDCl}_3$ ) and thia[29]annulene (14) (in  $\text{CD}_2\text{Cl}_2$ ) at room temperature.



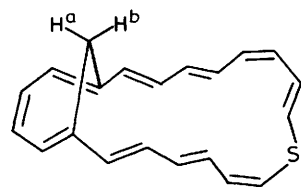
(7A)



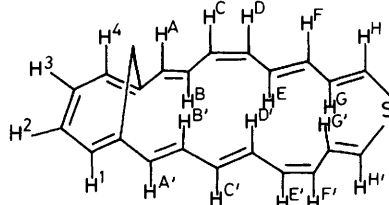
(8A)



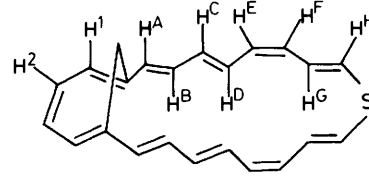
(9A)



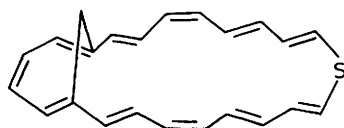
(10)



(11A)



(11B)



(11C)

the higher thia-annulenes, see below), the high-field half of the AB-pattern might be assigned to the bridge proton H<sup>a</sup> above the cycloheptatriene moiety, in consideration of its homoconjugative effect,<sup>7a,16</sup> and the shielding effect of the CH<sup>2</sup>=CH<sup>3</sup> double bond.

Analysis of the olefinic proton signals of 6,11-methanothia[17]annulene (**8**) (Figure 1) indicates that the molecule contains a diene moiety with a *Z, s-trans, E* sequence and a triene chain with *E, s-cis, Z, s-trans, E* sequence. Molecular model considerations suggest that the structure (**8A**) is the most reasonable among the four possible combinations of the two moieties. The olefinic inner protons resonate at high field, with the outer protons at low field, suggesting that the thia[17]annulene (**8A**) is diatropic, as expected of an 18 $\pi$ -electron system with lone pair electrons of the sulphur atom.

The olefinic proton signals of 8,13-methanothia[19]annulene (**9**) show that the compound has two triene moieties with *E, s-trans, Z, s-trans, E* sequence. Thus the structure (**9A**) is unambiguously given to this compound. The assignment of the chemical shifts for the triene chain depends on which of the two doublet signals is assigned to the proton adjacent to the sulphur atom. The doublet at higher field is assigned to the proton adjacent to the sulphur atom in consideration of its anisotropic effect, and the doublet at lower field is assigned to the proton adjacent to the cycloheptatriene ring (see Experimental section), owing to its homoconjugative effect.<sup>7a,16</sup> As is seen from Figure 1, the olefinic inner protons resonate at low field, while the outer protons at high field, suggesting that the thia[19]annulene (**9A**) is paratropic, as expected of a 20 $\pi$ -electron system. The methylene signal appears as a sharp singlet at room temperature, suggesting a rapid flipping of the methano-bridge. The dynamic NMR behaviour is discussed later.

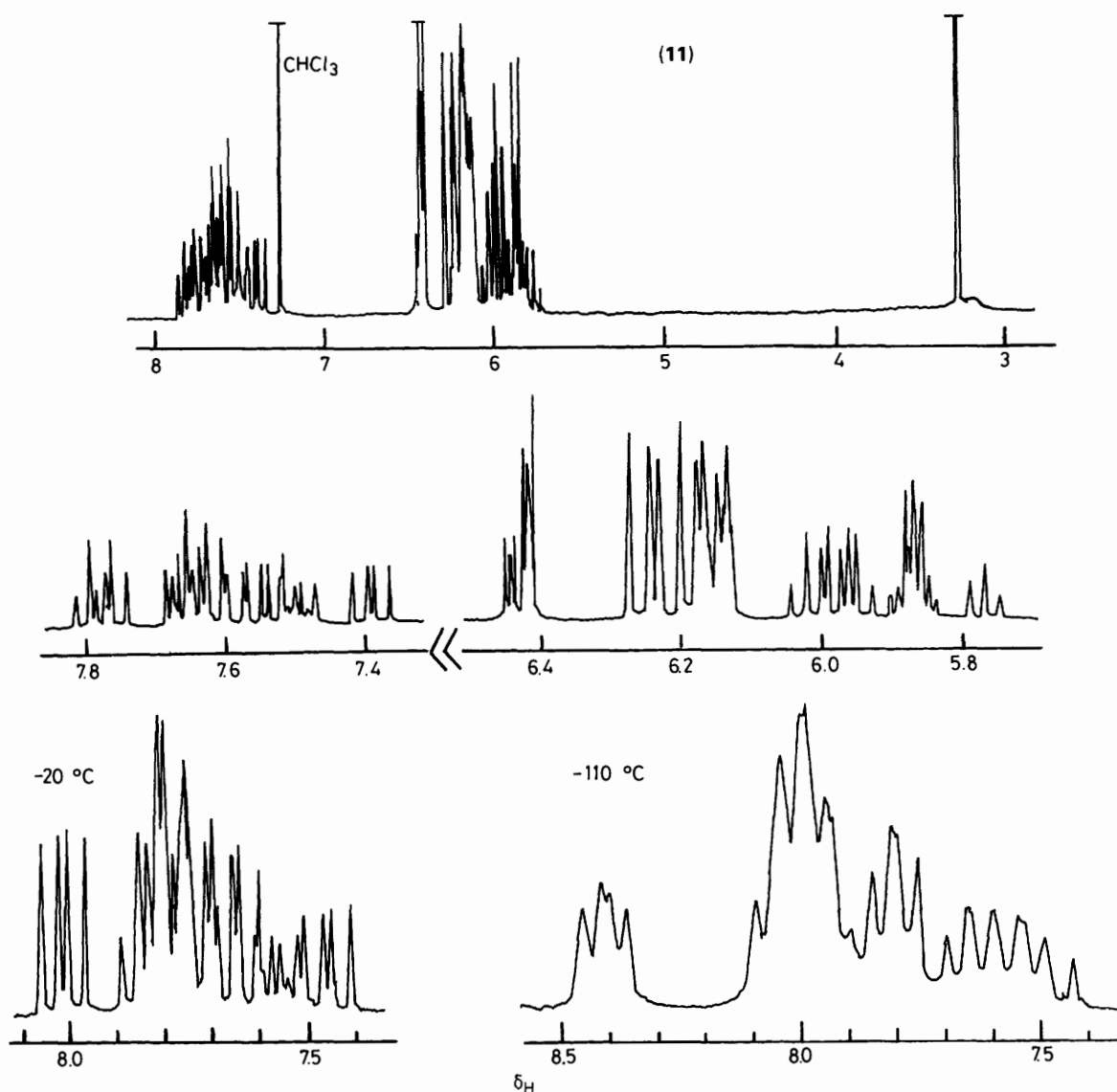
The olefinic proton signals of 8,13-methanothia[21]annulene (**10**) at room temperature is rather complex (Figure 1). Sixteen protons out of the eighteen olefinic protons appear between  $\delta$  6.0 and 7.0, and this hinders a first-order analysis. This also suggests that the thia[21]annulene (**10**) is atropic. Another possibility is the occurrence of fast interconversion between the

outer and inner protons on the NMR time-scale at room temperature. To test this possibility, variable-temperature spectra were examined. No spectral change suggestive of exchange broadening was observed down to  $-95^\circ\text{C}$ , although small shifts of the peaks within 0.5 ppm were detected. The most likely structure (**10**) from molecular model considerations is that shown.

All the compounds discussed so far are believed to exist as a single isomer, but those described below are shown to be a mixture of two or more isomers.

As is seen from Figure 2, the <sup>1</sup>H NMR spectrum of 10,15-methanothia[23]annulene (**11**) revealed that the compound is composed of two isomers; a sharp singlet and a broad singlet appear in the methylene proton region (see also Figure 3). The isomer ratio in CDCl<sub>3</sub> was 1.3–3.0 depending on the samples prepared under different conditions and slowly approached an equilibrium ratio of *ca.* 2.0 when left for several days at room temperature; this was accompanied by considerable thermal decomposition. We infer that the formation ratio upon synthesis is close to the equilibrium ratio and that the isomer ratio changes with the work-up processes including recrystallization. Attempts to separate the isomers have so far been unsuccessful. Preparative gel permeation chromatography gave a single broad peak even after 50 cycles. The initial and later parts of the peak showed slightly different isomer ratios.

Careful examination of the olefinic proton signals (the second spectrum from the top in Figure 2) shows that the two isomers are geometrical isomers in which the positions of the *Z*-double bonds are different. The unsymmetrical structure (**11A**) is unambiguously assigned to the major isomer. The symmetrical structure (**11B**) is tentatively assigned to the minor isomer, although another structure (**11C**), which seems to be more strained than (**11B**), based on Dreiding models inspection, cannot be completely excluded. In both isomers (**11A**) and (**11B**) the olefinic inner protons resonate at low field, with the outer protons at high field (the top spectrum in Figure 2), suggesting that these thia[23]annulenes are paratropic, as expected of a 24 $\pi$ -electron system.



**Figure 2.** 500 MHz  $^1\text{H}$  NMR spectra of a mixture of thia[23]annulene (11) and the olefinic proton region in  $\text{CDCl}_3$  at 20 °C, and 270 MHz  $^1\text{H}$  NMR spectra of the olefinic inner proton region in  $\text{CD}_2\text{Cl}_2$  at low temperature.

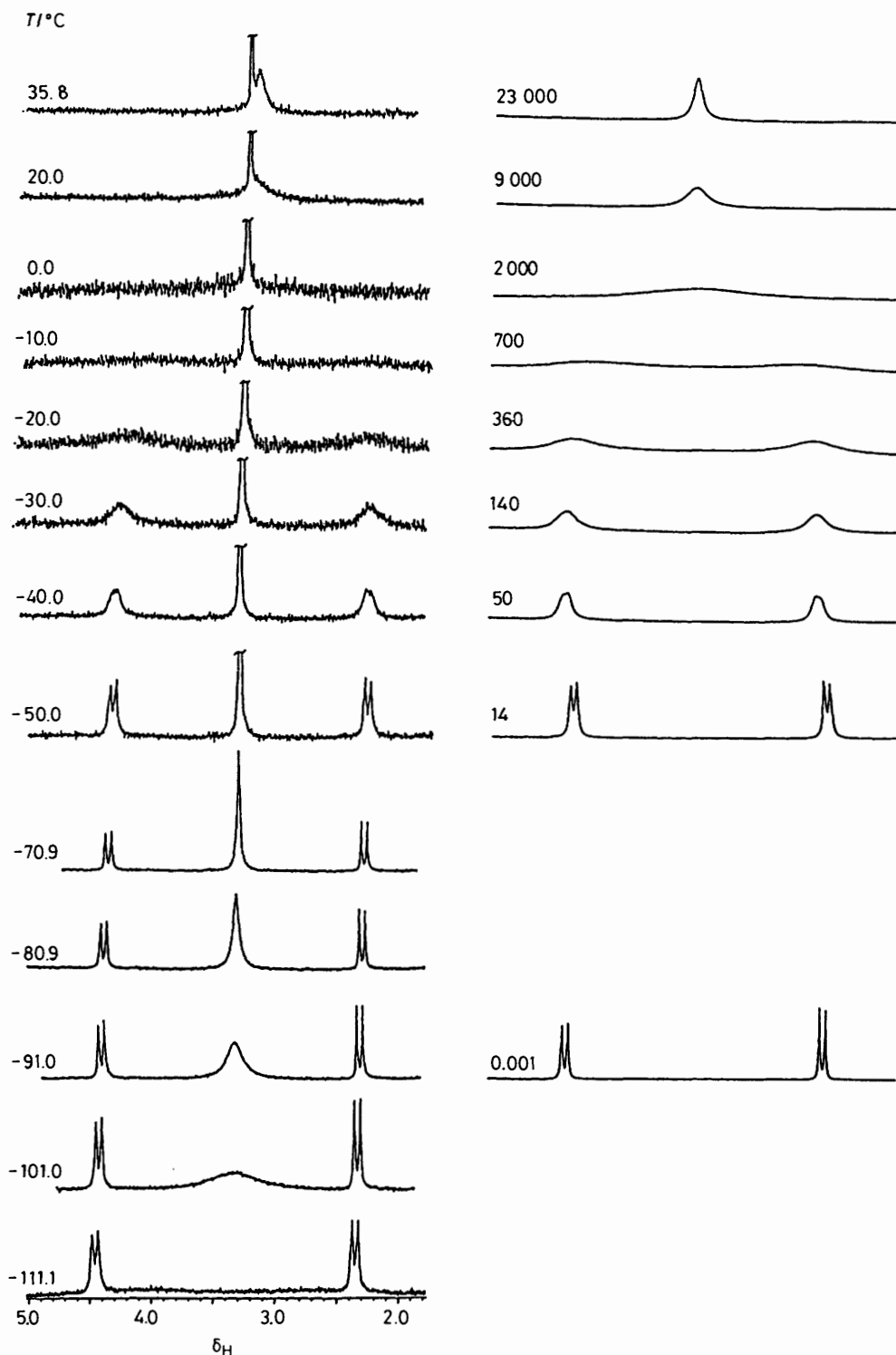
10,15-Methanothia[25]annulene (12) is shown to be a complex mixture of isomers. As indicated by the three labels A, B, and C in Figure 4, two singlets and an AB-quartet are present in the methylene proton region at room temperature and an extremely broad signal due to at least three more isomers, and appearing as the three AB-quartets (D, E, and F) is buried under the baseline at  $-60^\circ\text{C}$ . The thia[25]annulene (12) therefore consists of at least six isomers. The olefinic protons appear in the narrow region of  $\delta$  5.6–6.9 throughout the temperature range of 20 to  $-60^\circ\text{C}$ . This suggests that these thia[25]annulenes are atropic, but structural assignments for the isomers are impossible.

12,17-Methanothia[27]annulene (13) as obtained consists of two isomers, in the ratio 7:5, as evidenced from two singlets in the methylene proton region (Figure 5). However, the isomer ratio in  $\text{CD}_2\text{Cl}_2$  solution slowly approached an equilibrium ratio of *ca.* 1.5 when kept for four days at room temperature. The olefinic protons give rise to two groups of signals in the  $\delta$  7.5–6.8 and 6.5–5.8 regions in the intensity ratio 1:2, respectively, suggesting that these thia[27]annulenes are paratropic, as expected of  $28\pi$ -electron system, although structural assignments for the isomers are again impossible.

12,17-Methanothia[29]annulene (14) consists of at least two isomers as judged from the presence of two singlets in the methylene proton region at room temperature (Figure 1). Because of contamination by considerable amounts of decomposition products, variable-temperature measurements were abandoned. The appearance of the olefinic protons in such a narrow region suggests that these thia[29]annulenes are atropic.

Although the  $^1\text{H}$  NMR spectra of the 4,9:17,22-dimethano-1,14-dithia[26]annulene (15) and 6,11:21,26-dimethano-1,16-dithia[30]annulene (16) are not illustrated in the Figures, both the olefinic inner and outer protons resonate at almost the same field (see Experimental section), indicating that both the dithia[26]- and (15) and -[30]-annulene (16) are atropic. The fact that the methylene protons in both compounds (15) and (16) resonate as two singlets at different fields suggests that the flipping of the methylene bridge of the compounds (15) and (16) is fast on the NMR time-scale (see below) and that both (15) and (16) exist presumably in unsymmetrical structures.

Thus, the  $(4n + 2)\pi$ -electron methanothia-annulenes such as (10), (12), and (14) with unequal numbers of double bonds between the sulphur atom and the junctions with the cyclo-



**Figure 3.** 270 MHz variable-temperature  $^1\text{H}$  NMR spectra of the methylene protons of thia[23]annulene (**11**) in  $\text{CD}_2\text{Cl}_2$  (left) and the calculated spectra for the minor isomer (**11B**) (right).

heptatriene system, *i.e.* formally unsymmetrical thia-annulenes, do not show a ring-current effect, except that for thia[17]annulene (**8**), while the  $(4n)\pi$ -electron methanothia-annulenes such as (**9**), (**11**), and (**13**) with equal numbers of double bonds on both sides, *i.e.* formally symmetrical thia-annulenes, sustain a ring current, except for the thia(15)annulene (**7**).

*Flipping of the Methylene Bridge.*—In order to obtain information on the energy barriers for the flipping of the

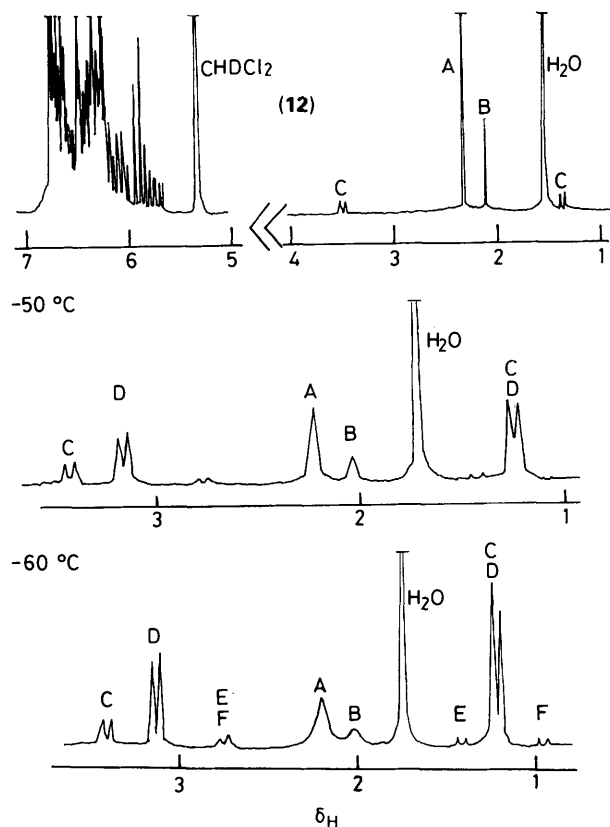
methano-bridge, variable-temperature  $^1\text{H}$  NMR studies were performed for the singly methano-bridged compounds except (**12**) and (**14**). The results are summarized in Table 1.

The methylene protons of compounds (**7**), (**8**), and (**10**) appear as an AB-quartet at room temperature, indicating that the flipping of the methano-bridge is slow on the NMR time-scale. In compound (**7**), the signal remains a sharp AB-quartet even at  $115^\circ\text{C}$  in  $[\text{}^2\text{H}_8]$  toluene, although rapid thermal decomposition of the sample occurs at high temperatures. This

**Table 1.** Calculated energies for flipping of the methylene protons.<sup>a</sup>

Compd.	Spectral data				Kinetic data			
	Chem. shift $\delta$	$J$ (Hz)	Temp. (°C)	$T_c^b$ (°C)	$\Delta H^\ddagger$ (kcal mol <sup>-1</sup> )	$\Delta S^\ddagger$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G^\ddagger$ (kcal mol <sup>-1</sup> )	Temp. (°C)
[15] (7) <sup>f</sup>	0.19, 2.65	12.5	20	$\geq 115$			$\geq 17.4$	
[17] (8) <sup>f</sup>	0.54, 2.07	13.2	20	120			$17.8 \pm 0.2$	(120)
[19] (9) <sup>g</sup>	2.54, 4.53	(13) <sup>c</sup>	-91	-65			$9.1 \pm 0.2$	(-65)
[21] (10) <sup>f</sup>	1.08, 2.89	12.9	20	$> 110$			$> 17.4$	
[23] (11A) <sup>g</sup>	3.29		20	-110			7.1	(-110)
(11B) <sup>g</sup>	2.35, 4.45	13.2	-111	-5	$11.2 \pm 0.4$	$-2.2 \pm 1.6$	$11.6_g$	(-70)
[27] (13A) <sup>d</sup>	3.09		20	$< -100$			$< 7.5$	
(13B) <sup>e</sup>	2.22, 4.22	(13) <sup>c</sup>	-100	-70			$8.9 \pm 0.2$	(-70)

<sup>a</sup> Taken at 270 MHz. <sup>b</sup> Coalescence temperature. Reliable to  $\pm 5^\circ\text{C}$ . <sup>c</sup> Assumed. <sup>d</sup> Major isomer. <sup>e</sup> Minor isomer. <sup>f</sup> In  $[\text{D}_8]\text{toluene}$ . <sup>g</sup> In  $\text{CD}_2\text{Cl}_2$ .



**Figure 4.** 270 MHz  $^1\text{H}$  NMR spectra of thia[25]annulene (12) at 20 °C and the methylene proton region at low temperature in  $\text{CD}_2\text{Cl}_2$ .

indicates that the flipping barrier is far higher than  $17.4 \text{ kcal mol}^{-1}$ . The methylene signal of compound (8) coalesces at about  $120^\circ\text{C}$  and the free energy of activation for the flipping is estimated to be  $17.8 \text{ kcal mol}^{-1}$  at  $120^\circ\text{C}$ . Also, in compound (10), the methylene signal is extensively broadened at  $110^\circ\text{C}$ , suggesting a similar barrier height as for compound (8).

The methylene protons of compound (9) give a singlet at room temperature, suggesting rapid flipping of the methano-bridge. Upon lowering the temperature, the signal broadens and splits into two peaks at  $-65^\circ\text{C}$ . The slow-exchange-limit spectrum was not obtained, even at the lowest temperature of  $-91^\circ\text{C}$ . The free energy of activation at the coalescence temperature was estimated to be  $9.1 \pm 0.2 \text{ kcal mol}^{-1}$ .

In the thia[23]annulene (11) the dynamic NMR behaviour

depends on the isomers. As is seen from Figure 3, the methylene signal of the minor isomer (11B) appears as a very broad signal at room temperature, but as an AB-quartet at  $-110^\circ\text{C}$ . Total lineshape analysis of the spectra in the temperature range of  $36$  to  $-15^\circ\text{C}$  using the DNMR3 program<sup>17</sup> gave the kinetic parameters shown in Table 1. The methylene proton signal of the major isomer (11A) appears as a sharp singlet at room temperature, which broadens on lowering the temperature and disappears under the baseline at  $-111^\circ\text{C}$ , the lowest attainable temperature. The free energy of activation for this process is estimated to be  $7.1 \text{ kcal mol}^{-1}$  at  $-111^\circ\text{C}$  if the same chemical-shift difference as that of (11B) is assumed.

In the thia[27]annulene (13) the methylene signal of the minor isomer decoalesces into an AB-quartet at  $-70^\circ\text{C}$  (Figure 5), affording a value for the free energy barrier of  $8.9 \text{ kcal mol}^{-1}$ . The methylene signal of the major isomer is still a broad singlet at  $-100^\circ\text{C}$  (Figure 5), suggesting a lower barrier.

The parent cyclohepta-1,3,5-triene adopts a boat conformation and ring inversion is reported to have an energy barrier of  $6.1 \text{ kcal mol}^{-1}$ .<sup>18</sup> In methanoannulenes, where a long chain is connected at both terminals to the cycloheptatriene moiety, the flipping of the methylene bridge is accompanied by the inversion of the cycloheptatriene moiety, and the energy barrier should be governed by the strain of the macrocycle in both the ground and transition states, which in turn depends on the ring size and the rigidity of the macrocycle.

Table 1 shows that the flipping barriers in the methanothiaannulenes examined are always higher than that of cycloheptatriene and that, roughly speaking, the barrier decreases as the ring size increases. This is intuitively understood since the flexibility of the macrocycle is expected to increase with ring size. Of course, the ring size is not the only factor as is shown from the comparison of the energy of compound (9) with that of compound (10). In this connection, the large difference in the energy barriers between the two isomers in compounds (11) and (13) is interesting. Since the structure of the isomers of compound (13) are not clear, we will focus our attention on compound (11). The temperature dependence of the olefinic proton chemical shifts in compound (11) seems to give some indication on this point. The inner proton signals shift downfield and the outer proton ones shift upfield on lowering the temperature (two spectra at the bottom of Figure 2). The degree of movement is larger in the minor isomer (11B) than in the major isomer (11A). For example,  $\text{H}^{\text{D}}$  of (11B), which appears at  $\delta 7.81$  at  $20^\circ\text{C}$  in  $\text{CD}_2\text{Cl}_2$ , moves to  $\delta 8.41$  at  $-111^\circ\text{C}$ , while  $\text{H}^{\text{D}}$  of (11A) appears at  $\delta 7.53$  at  $20^\circ\text{C}$  and at  $\delta 7.64$  at  $-110^\circ\text{C}$ . This suggests that (11B) has a higher rigidity for its molecular skeleton to accommodate higher paratropicity while (11A) is far more flexible. Structure (11A) may therefore more easily relieve the strain at the transition

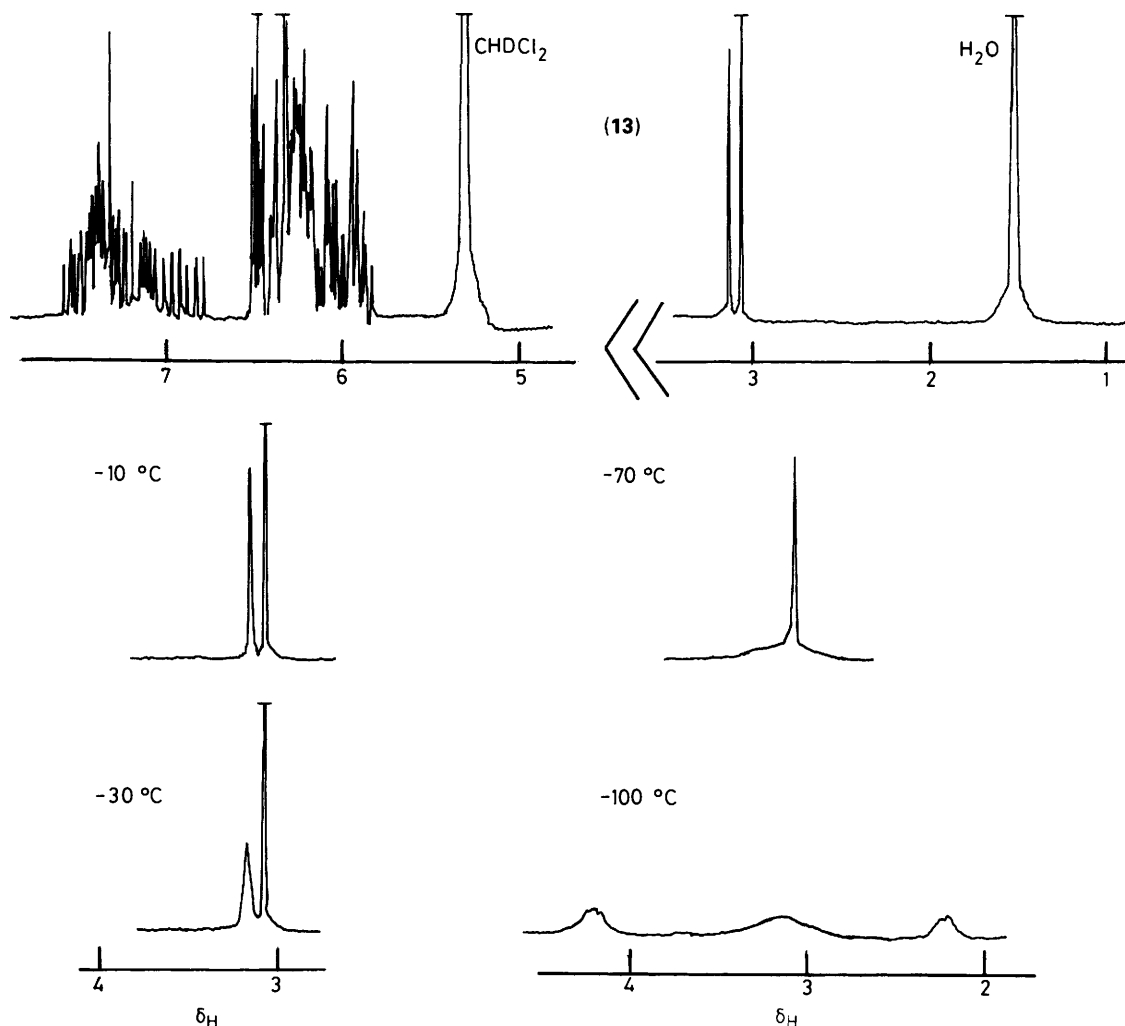


Figure 5. 270 MHz  $^1\text{H}$  NMR spectra of thia[27]annulene (13) at 22 °C and the methylene proton region at low temperature in  $\text{CD}_2\text{Cl}_2$ .

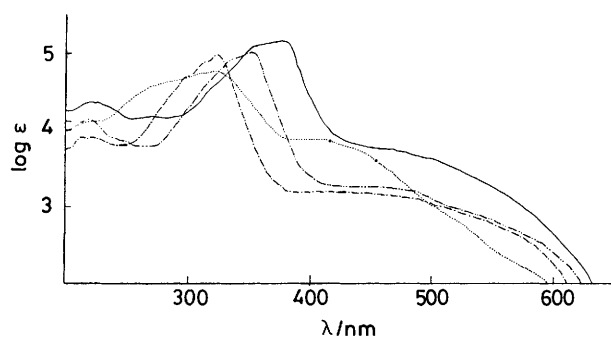
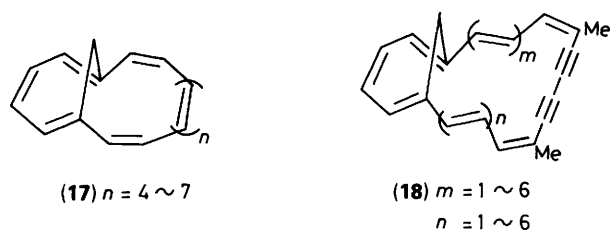


Figure 6. Electronic absorption spectra of thia-[17]- (8) (----), [19]- (9) (---), [23]- (11) (- - -), and -[27]-annulene (13) (—) in THF.

state of the methylene flipping and hence have a lower barrier than isomer (11B).

It was previously shown that the methanoannulene system (17) exhibits high conformational mobility, and both the methylene flipping and the interconversion between the olefinic inner and outer protons has been observed.<sup>8</sup> In contrast, the tetrahydromethanoannulene system (18) shows high conformational stability for its molecular skeleton, of which  $^1\text{H}$  NMR spectra did not show temperature dependency.<sup>7</sup> On the other hand, the flipping of the methylene protons occurs in some of



the thia-annulenes in this study, but the interconversion between the olefinic inner and outer protons was not detected. Therefore, the rigidity of the molecular skeleton among these three systems decreases in the order of the tetrahydromethanoannulenes (18) > the methanothia-annulenes (7)–(14) > the methanoannulenes (17).

**Electronic Spectra.**—The electronic absorption maxima of the thia-annulenes (7)–(16) are listed in Table 2, and the absorption spectra of the methanothia-[17]- (8), -[19]- (9), -[23]- (11), and -[27]-annulene (13) which show the ring-current effect are illustrated in Figure 6. As seen from Figure 6, the spectra of the  $(4n)\pi$ -electron thia-annulenes (9), (11), and (13) are similar in shape and exhibit some broadening of the absorption curves, as compared with the spectrum of the  $(4n + 2)\pi$ -electron, thia[17]annulene (8), as has been observed



**Table 2.** Electronic absorption maxima of the methanothia-annulenes (7)–(14), and the dimethanodithia-annulenes (15) and (16) in THF [ $\lambda_{\max}$ (nm)( $\epsilon_{\max}$ )]. The strongest absorptions of compounds (8) and (9) are indicated in bold type.

[15]	(7): 248sh (18 400), 286 (51 000), 345sh (4 750)
[17]	(8): 290sh (43 900), <b>320 (57 500)</b> , 400 (7 400)
[19]	(9): 298sh (47 800), 312sh (70 100), <b>323 (92 000)</b>
[21]	(10): 326sh (49 000), 335 (51 500), 455sh (3 160)
[23]	(11): 340sh (82 700), 352 (98 000), 463sh (1 700)
[25]	(12): 364 (73 300), 451sh (5 990)
[27]	(13): 364sh (96 500), 377 (104 000), 478sh (7 390)
[29]	(14): 369sh (86 700), 379 (91 500)
Dithia[26]	
[15]	(15): 278 (51 600), 298sh (45 500), 337 (34 100)
[30]	(16): 285 (55 800), 321 (54 000), 352 (66 600)

in the carbocyclic annulene series.<sup>19</sup> Table 2 shows that each band exhibits a bathochromic shift as the ring size increases; however, the main maximum of the diatropic thia[17]annulene (8) is very close to that of the paratropic thia[19]annulene (9). Thus, it is evident that the same alternation in the wavelengths of the main electronic absorption maxima between  $(4n + 2)$  and  $(4n)$  systems occurs in these methanothia-annulenes, as has already been demonstrated for monocyclic annulenes and dehydroannulenes.<sup>20</sup>

**Summary.**—The limiting size showing a ring-current effect is predicted to be smaller in heteroannulenes than that in annulenes, since the tropicity of the former is found to be much less than that of annulenes.<sup>1</sup> However, it was found that the methanothia-annulenes show ring-current effect up to the large 27-membered ring in the formally symmetrical,  $(4n)\pi$ -electron system, presumably due to the presence of the methano-bridge which serves to keep the thia-annulene perimeter rigid.<sup>9</sup>

## 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 THF 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. <sup>1</sup>H NMR spectra were recorded as CDCl<sub>3</sub> solutions, unless otherwise stated, with a JEOL FX-90Q (90 MHz), a JEOL GX-270 (270 MHz), or a Bruker AM-500 (500 MHz) spectrometer, SiMe<sub>4</sub> being used as internal standard. Assignments were clarified by the use of decoupling experiments where necessary. Merck alumina (activity II–III) and Merck silica gel 60 were used for column chromatography. Compounds were preadsorbed from hexane, ether, or dichloromethane solution onto the adsorbent before column chromatography on the same adsorbent. Gel permeation chromatography was performed on an LC-09 Liquid Chromatograph from Japan Analytical Industry Co., Ltd. using a series of JAIGEL H1 and H2 columns and chloroform as the eluant. All the Wittig reactions were carried out under a nitrogen or argon atmosphere. 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.

**The Isomeric 6-(10-Formyldeca-1,3,5,7,9-pentaenyl)-1-(8-formylocta-1,3,5,7-tetraenyl)cyclohepta-1,3,5-triene (3j) and (3j').**—A solution of lithium ethoxide prepared from lithium (694 mg, 100 mmol) in dry ethanol (171 ml) was added dropwise

during 2.5 h to a stirred solution of 1-(6-formylhexa-1,3,5-trienyl)-6-(8-formylocta-1,3,5,7-tetraenyl)cyclohepta-1,3,5-triene (3h)<sup>7b</sup> (4.14 g, 12.5 mmol) and the salt (5)<sup>10</sup> (35.0 g, 81.4 mmol) in DMF (406 ml) at 70 °C. After being stirred for a further 1 h at 70 °C, the mixture was cooled to room temperature, poured onto water, and extracted with benzene. After removal of the solvent, the residue was chromatographed on alumina (4.2 × 7.7 cm). The fractions containing the bisacetal (6), eluted with 50–80% benzene in hexane, were collected and evaporated. The residue was dissolved in THF (180 ml), and the solution was admixed with ethanol (58 ml) and 0.5M-hydrochloric acid (88 ml), and the mixture was stirred for 30 min at room temperature. Then the mixture was poured onto water, and the aqueous layer was extracted with benzene. The combined organic layer was washed with aqueous sodium hydrogen carbonate, and dried. The residue was chromatographed on silica gel (4.2 × 14.0 cm). The fractions eluted with 50–60% benzene in dichloromethane afforded the dialdehyde (3j') and its stereoisomers (3.85 g, 75%). Recrystallization from hexane–benzene formed the *mono-Z-isomer* (3j') as dark purple needles, m.p. 110–112 °C (decomp.); *m/z* 382 (*M*<sup>+</sup>, 66%) and 91 (100); *M*, 382.4;  $\lambda_{\max}$  370sh ( $\epsilon$  84 600), 392 (95 100), and 493sh nm (19 700);  $\nu_{\max}$  1 680 (CHO), 1 610 (C=C), 1 010, 1 000 (*E*-HC=CH), and 740 cm<sup>-1</sup> (*Z*-HC=CH);  $\delta$  (90 MHz) 10.16 (1 H, d, *J* 8 Hz, CHO<sup>a</sup>), 9.57 (1 H, d, *J* 8 Hz, CHO<sup>b</sup>), 7.31–6.36 (20 H, m, olefinic and 7-membered-ring H), 6.16 (1 H, dd, *J* 15 and 8 Hz, H<sup>H</sup>), 5.87 (1 H, dd, *J* 10 and 8 Hz, H<sup>I</sup>), and 2.73 (2 H, s, CH<sub>2</sub>) (Found: C, 84.2; H, 6.9. C<sub>27</sub>H<sub>26</sub>O<sub>2</sub> requires C, 84.8; H, 6.85%). Attempts to improve the elemental analysis failed.

**Isomerization of *Z*-compound (3j') to *E*-Isomer (3j).**—To a stirred solution of the dialdehyde (3j') (178 mg, 0.465 mmol) in dichloromethane (110 ml) was added iodine (0.2 g) in one portion. The solution was stirred overnight at room temperature. Then the solution was washed with 5% aqueous sodium thiosulphate and dried. After removal of the solvent, the residue was chromatographed on silica gel (3.2 × 5.5 cm). The fractions eluted with 60–80% benzene in dichloromethane afforded the isomerized *di-E-isomer* (3j) (85 mg, 48%). It formed dark purple needles, m.p. 83–84 °C (decomp.) (from benzene); *m/z* 382 (*M*<sup>+</sup>, 56%) and 78 (100); *M*, 382.4;  $\lambda_{\max}$  378sh ( $\epsilon$  106 000), 393 (117 000), and 481sh nm (25 300);  $\nu_{\max}$  1 680 (CHO), 1 610 (C=C), 1 010 and 1 000 cm<sup>-1</sup> (*E*-HC=CH);  $\delta$  (90 MHz) 9.57 (2 H, d, *J* 8 Hz, CHO), 7.16 (2 H, dd, *J* 15 and 11 Hz, H<sup>G</sup> and H<sup>I</sup>), 6.90–6.30 (18 H, m, olefinic and 7-membered-ring H), 6.17 (2 H, dd, *J* 15 and 8 Hz, H<sup>H</sup> and H<sup>I</sup>), and 2.73 (2 H, s, CH<sub>2</sub>) (Found: C, 85.0; H, 7.0. calc. for C<sub>27</sub>H<sub>26</sub>O<sub>2</sub>: C, 84.8; H, 6.85%).

**4,9:17,22-Dimethano-1,14-dithia[26]annulene (15).**—A solution of lithium ethoxide prepared from lithium (179 mg, 25.6 mmol) in dry ethanol (100 ml) was added dropwise during 4.5 h to a stirred solution of the dialdehyde (3b)<sup>7a</sup> (1.87 g, 10.7 mmol) and the salt (4a)<sup>4</sup> (9.50 g, 12.8 mmol) in DMF (150 ml) at 75 °C. After being stirred for a further 30 min at 75 °C, the solution was cooled to room temperature, poured onto water, and then extracted with benzene. The extracts were washed and dried. The residue after removal of solvent was passed through a short column of alumina (4.2 × 5.0 cm). The fractions eluted with ether (400 ml) were collected and evaporated. The residue was chromatographed on alumina (4.2 × 12.0 cm). The initial fractions eluted with 5–20% ether in hexane afforded unidentified material (179 mg) as a red liquid. The following fractions eluted with 30–50% ether in hexane afforded the *dimethanodithia*[26]annulene (15) (117 mg, 2.7%). It formed yellow needles, m.p. 186–188 °C (decomp.) (from hexane–benzene); *m/z* 400 (*M*<sup>+</sup>, 27%) and 115 (100); *M*, 400.6; for UV data see Table 2;  $\nu_{\max}$  960 (*E*-HC=CH), 740 and 720 cm<sup>-1</sup> (*Z*-

HC=CH);  $\delta$  (270 MHz) 7.24 (2 H, dd,  $J$  15 and 11 Hz, olefinic H), 6.91–6.11 (18 H, m, olefinic and 7-membered-ring H), 3.08 (2 H, s, CH<sub>2</sub>), and 2.61 (2 H, s, CH<sub>2</sub>) (Found: C, 77.6; H, 6.0. C<sub>26</sub>H<sub>24</sub>S<sub>2</sub> requires C, 77.95, H, 6.0%).

**6,11-Methanothia[15]annulene (7A) and 6,11:21,26-Dimethano-1,16-dithia[30]annulene (16).**—A solution of lithium ethoxide prepared from lithium (139 mg, 20.5 mmol) in dry ethanol (150 ml) was added dropwise during 3.5 h to a stirred solution of the salt (4a) (7.44 g, 9.94 mmol) and the dialdehyde (3c)<sup>7a</sup> (2.00 g, 9.19 mmol) in DMF (400 ml) at 70 °C. After being stirred for a further 1.5 h at 70 °C, the mixture was worked up as for the isolation of compound (15). The product was chromatographed on alumina (3.8 × 12.0 cm). The initial fractions eluted with 5–10% benzene in hexane afforded the *methanothia[15]annulene* (7A) (118 mg, 5.2%). It formed yellow needles, m.p. 109–110 °C (from hexane);  $m/z$  226 ( $M^+$ , 78%) and 191 (100);  $M$ , 226.3; for UV data see Table 2;  $\nu_{\max}$  970 (*E*-HC=CH), 745, and 715 cm<sup>-1</sup> (*Z*-HC=CH);  $\delta$  (500 MHz) 7.12–7.04 (2 H, m, H<sup>2</sup> and H<sup>3</sup>), 6.86 (2 H, dd,  $J$  11 and 8 Hz, H<sup>C</sup>), 6.78–6.70 (2 H, br s, H<sup>1</sup> and H<sup>4</sup>) 6.67 (2 H, d,  $J$  16 Hz, H<sup>A</sup>), 6.47 (2 H, dd,  $J$  16 and 11 Hz, H<sup>B</sup>), 5.66 (2 H, d,  $J$  8 Hz, H<sup>D</sup>), 2.66 (1 H, d,  $J$  13 Hz, H<sup>b</sup>), and 0.19 (1 H, d,  $J$  13 Hz, H<sup>a</sup>) (see Figure 1) (Found: C, 79.5; H, 6.2. C<sub>15</sub>H<sub>14</sub>S requires C, 79.6; H, 6.2%).

The following fractions eluted with 35–45% benzene in hexane afforded the *dimethanodithia[30]annulene* (16) (235 mg, 10.4%). It formed orange needles, m.p. 207–210 °C (decomp.) (from hexane–benzene);  $m/z$  452 ( $M^+$ , 41%) and 165 (100);  $M$ , 452.6; for UV data see Table 2;  $\nu_{\max}$  970 (*E*-HC=CH), 740, and 730 cm<sup>-1</sup> (*Z*-HC=CH);  $\delta$  (270 MHz) 7.05–5.96 (24 H, m, olefinic H), 2.83 (2 H, s, CH<sub>2</sub>), and 2.66 (2 H, s, CH<sub>2</sub>) (Found: C, 79.75; H, 6.2. C<sub>30</sub>H<sub>28</sub>S<sub>2</sub> requires C, 79.6; H, 6.2%).

**6,11-Methanothia[17]annulene (8A).**—A solution of the dialdehyde (3d)<sup>7a</sup> (2.53 g, 11.2 mmol) in DMF (180 ml) and a solution of lithium ethoxide prepared from lithium (206 mg, 29.0 mmol) in dry ethanol (180 ml) were simultaneously added dropwise during 4 h to a stirred solution of the salt (4a) (10.9 g, 14.5 mmol) in DMF (298 ml) at 70 °C. After being stirred for a further 1 h at 70 °C, the mixture was worked up as for the isolation of compound (15). The product was passed through a short column of alumina (4.2 × 5.5 cm). The fractions eluted with dichloromethane (400 ml) were collected and evaporated. The residue was chromatographed on alumina (3.7 × 21.0 cm). The fractions eluted with 2–10% ether in hexane were collected and evaporated. The residue was again chromatographed on alumina (3.2 × 10.5 cm). The fractions eluted with 20% benzene in hexane afforded the *methanothia[17]annulene* (8A) (45 mg, 1.6%). It formed red needles, m.p. 120–121 °C (from hexane);  $m/z$  252 ( $M^+$ , 40%) and 115 (100);  $M$ , 252.3; for UV data see Table 2 and Figure 6;  $\nu_{\max}$  975 (*E*-HC=CH), 740, and 705 cm<sup>-1</sup> (*Z*-HC=CH);  $\delta$  (500 MHz) 7.05–6.94 (2 H, m, H<sup>2</sup> and H<sup>3</sup>), 6.97 (1 H, d,  $J$  15 Hz, H<sup>A</sup>), 6.97 (1 H, d,  $J$  15 Hz, H<sup>A</sup>), 6.93 (1 H, dd,  $J$  11 and 10 Hz, H<sup>C</sup>), 6.74 (1 H, d,  $J$  6 Hz, H<sup>1</sup> or H<sup>4</sup>), 6.68 (1 H, d,  $J$  6 Hz, H<sup>4</sup> or H<sup>1</sup>), 6.68 (1 H, t,  $J$  11 Hz, H<sup>C</sup>), 6.46 (1 H, d,  $J$  10 Hz, H<sup>D</sup>), 6.45 (1 H, dd,  $J$  16 and 5 Hz, H<sup>E</sup>), 6.26 (1 H, dd,  $J$  11 and 5 Hz, H<sup>D</sup>), 5.64 (1 H, dd,  $J$  15 and 11 Hz, H<sup>B</sup>), 5.12 (1 H, dd,  $J$  15 and 11 Hz, H<sup>B</sup>), 4.52 (1 H, d,  $J$  16 Hz, H<sup>F</sup>), 2.39 (1 H, d,  $J$  13 Hz, H<sup>b</sup>), and 0.67 (1 H, d,  $J$  13 Hz, H<sup>a</sup>) (see Figure 1) (Found: C, 80.7; H, 6.7. C<sub>17</sub>H<sub>16</sub>S requires C, 80.9; H, 6.4%).

**8,13-Methanothia[19]annulene (9A).**—A solution of the dialdehyde (3e)<sup>7b</sup> (1.21 g, 4.80 mmol) in DMF (150 ml) and a solution of lithium ethoxide prepared from lithium (82 mg, 11.6 mmol) in dry ethanol (40 ml) were simultaneously added dropwise during 3 h to a stirred solution of the salt (4a) (4.30 g, 5.80 mmol) in DMF (150 ml) at 65 °C. After being stirred for a further 30 min at 65 °C, the mixture was worked up as for the

isolation of compound (15). The product was passed through a short column of silica gel (4.0 × 3.0 cm). The fractions eluted with dichloromethane (400 ml) were collected and evaporated. The residue was chromatographed on alumina (3.2 × 15.6 cm). The fractions eluted with 30–50% benzene in hexane afforded the *methanothia[19]annulene* (9A) (18 mg, 1.4%). It formed dark red needles, m.p. 127–128 °C (from hexane–benzene);  $m/z$  278 ( $M^+$ , 82%) and 115 (100);  $M$ , 278.4; for UV data see Table 2 and Figure 6;  $\nu_{\max}$  940 (*E*-HC=CH) and 740 cm<sup>-1</sup> (*Z*-HC=CH);  $\delta$  (270 MHz) 8.39 (2 H, dd,  $J$  15 and 10 Hz, H<sup>E</sup>), 8.08 (2 H, dd,  $J$  15 and 10.5 Hz, H<sup>B</sup>), 6.41–6.38 (2 H, m, H<sup>2</sup>), 6.19 (2 H, d,  $J$  15 Hz, H<sup>A</sup>), 6.13–6.11 (2 H, m, H<sup>1</sup>), 5.95 (2 H, d,  $J$  15 Hz, H<sup>F</sup>), 5.91 (2 H, t,  $J$  10.5 Hz, H<sup>C</sup>), 5.84 (2 H, t,  $J$  10 Hz, H<sup>D</sup>), and 3.47 (2 H, s, CH<sub>2</sub>) (see Figure 1) (Found: C, 81.8; H, 6.6. C<sub>19</sub>H<sub>18</sub>S requires C, 82.0; H, 6.5%).

**8,13-Methanothia[21]annulene (10).**—A solution of lithium methoxide prepared from lithium (30.2 mg, 4.32 mmol) in dry methanol (40 ml) was added dropwise during 3.5 h to a stirred solution of the salt (4a) (1.62 g, 2.16 mmol) and the dialdehyde (3f)<sup>7b</sup> (500 mg, 1.80 mmol) in DMF (110 ml) at room temperature. After being stirred for a further 1 h at room temperature, the mixture was worked up as for the isolation of compound (15). The product was passed through a short column of alumina (4.2 × 6.0 cm). The fractions eluted with ether (400 ml) were collected and evaporated. The residue was chromatographed on alumina (3.7 × 17.6 cm). The fractions eluted with 30–40% ether in hexane afforded the *methanothia[21]annulene* (10) (21 mg, 3.8%). It formed orange needles, m.p. 181–183 °C (from hexane–benzene);  $m/z$  304 ( $M^+$ , 52%) and 91 (100);  $M$ , 304.4; for UV data see Table 2;  $\nu_{\max}$  990 (*E*-HC=CH), 730, and 705 cm<sup>-1</sup> (*Z*-HC=CH);  $\delta$  (270 MHz) 6.87–6.10 (16 H, m, olefinic and 7-membered-ring H), 5.92 (1 H, dd,  $J$  9 and 5 Hz, olefinic H), 5.47 (1 H, d,  $J$  16 Hz, olefinic H), 3.08 (1 H, d,  $J$  13 Hz, H<sup>b</sup>), and 1.06 (1 H, d,  $J$  13 Hz, H<sup>a</sup>) (see Figure 1) (Found: C, 82.35; H, 6.6. C<sub>21</sub>H<sub>20</sub>S requires C, 82.85; H, 6.6%). Attempts to improve the elemental analysis failed.

**The Isomeric 10,15-Methanothia[23]annulenes (11A) and (11B).**—A solution of lithium ethoxide prepared from lithium (77.7 mg, 11.1 mmol) in dry ethanol (75 ml) was added dropwise during 4.5 h to a stirred solution of the salt (4a) (4.14 g, 5.56 mmol) and the dialdehyde (3g)<sup>7b</sup> (1.41 g, 4.63 mmol) in DMF (200 ml) at 70 °C. After being stirred for a further 1.5 h at 70 °C, the mixture was worked up as for the isolation of compound (15). The product was passed through a short column of alumina (4.2 × 4.5 cm). The fractions eluted with ether (300 ml) were collected and evaporated. The residue was chromatographed on alumina (3.3 × 14.5 cm). The fractions eluted with 30–50% ether in hexane afforded a mixture of the *methanothia[23]annulenes* (11A) and (11B) (99 mg, 6.5%). It formed dark purple needles, m.p. 173–174 °C (decomp.) (from hexane–benzene);  $m/z$  330 ( $M^+$ , 100%);  $M$ , 330.4; for UV data see Table 2 and Figure 6;  $\nu_{\max}$  960 (*E*-HC=CH), 740 and 730 cm<sup>-1</sup> (*Z*-HC=CH) (Found: C, 83.25, H, 6.65. C<sub>23</sub>H<sub>22</sub>S requires C, 83.6; H, 6.7%); isomer (11A):  $\delta$  (500 MHz) 7.77 (1 H, dd,  $J$  15 and 11 Hz, H<sup>G</sup>), 7.66 (1 H, dd,  $J$  15 and 9 Hz, H<sup>B</sup>), 7.60 (1 H, dd,  $J$  14 and 11 Hz, H<sup>D</sup>), 7.55 (1 H, dd,  $J$  15 and 10 Hz, H<sup>B</sup>), 7.50 (1 H, dd,  $J$  15 and 10 Hz, H<sup>E</sup>), 7.39 (1 H, dd,  $J$  15 and 11 Hz, H<sup>G</sup>), 6.42 (2 H, m, H<sup>2</sup> and H<sup>3</sup>), 6.26 (2 H, d,  $J$  15 Hz, H<sup>H</sup> and H<sup>H</sup>), 6.22 (1 H, d,  $J$  15 Hz, H<sup>A</sup>), 6.20–6.10 (4 H, m, H<sup>1</sup>, H<sup>4</sup>, H<sup>C</sup>, and H<sup>F</sup>), 6.03 (1 H, t,  $J$  11 Hz, H<sup>F</sup>), 5.98 (1 H, d,  $J$  15 Hz, H<sup>A</sup>), 5.95 (1 H, t,  $J$  11 Hz, H<sup>E</sup>), 5.91–5.84 (2 H, m, H<sup>C</sup> and H<sup>D</sup>), and 3.28 (2 H, s, CH<sub>2</sub>) (see Figures 2 and 3); isomer (11B):  $\delta$  (500 MHz) 7.79 (2 H, dd,  $J$  15 and 10 Hz, H<sup>D</sup>), 7.65 (2 H, dd,  $J$  15 and 11 Hz, H<sup>G</sup>), 7.63 (2 H, dd,  $J$  15 and 11 Hz, H<sup>B</sup>), 6.45–6.40 (2 H, m, H<sup>2</sup>), 6.22 (2 H, d,  $J$  15 Hz, H<sup>H</sup>), 6.15–6.13 (6 H, m, H<sup>1</sup>, H<sup>A</sup>, and H<sup>C</sup>), 5.87 (2 H, t,

$J$  11 Hz,  $H^F$ ), 5.77 (2 H, t,  $J$  11 Hz,  $H^E$ ), and 3.25 (2 H, br s,  $CH_2$ ) (see Figures 2 and 3).

**10,15-Methanothia[25]annulene (12).**—A solution of lithium ethoxide prepared from lithium (108 mg, 15.3 mmol) in dry ethanol (103 ml) was added dropwise during 4.5 h to a stirred solution of the salt (**4a**) (5.68 g, 7.63 mmol) and the dialdehyde (**3h**)<sup>7b</sup> (2.10 g, 6.36 mmol) in DMF (300 ml) at 70 °C. After being stirred for a further 1 h at 70 °C, the mixture was worked up as for the isolation of compound (**15**). The product was passed through a short column of alumina (4.2 × 4.0 cm). The fractions eluted with ether (600 ml) were collected and evaporated. The residue was chromatographed on alumina (3.8 × 7.0 cm). The fractions eluted with 50% hexane in benzene afforded the *methanothia[25]annulene* (**12**) (33 mg, 1.5%). It formed brown needles, m.p. 187–188 °C (decomp.) (from hexane–benzene);  $m/z$  356 ( $M^+$ , 13%) and 324 (100);  $M$ , 356.5; for UV data see Table 2;  $\nu_{max}$  995, 960 ( $E-HC=CH$ ), 730 and 710  $cm^{-1}$  ( $Z-HC=CH$ );  $\delta$  (270 MHz) 6.90–5.65 (m, olefinic H), 3.48 (d,  $J$  12 Hz,  $CH_2$ ) 2.32 (s,  $CH_2$ ), 2.12 (s,  $CH_2$ ), and 1.38 (d,  $J$  12 Hz,  $CH_2$ ) (see Figure 4) (Found: C, 84.4; H, 7.0.  $C_{25}H_{24}S$  requires C, 84.2; H, 6.8).

**12,17-Methanothia[27]annulene (13).**—A solution of lithium ethoxide prepared from lithium (103 mg, 14.9 mmol) in dry ethanol (100 ml) was added dropwise during 4 h to a stirred solution of the salt (**4a**) (5.54 g, 7.44 mmol) and the dialdehyde (**3i**)<sup>7b</sup> (2.21 g, 6.20 mmol) in DMF (300 ml) at 70 °C. After being stirred for 1.5 h at 65 °C, the mixture was worked up as for the isolation of compound (**15**). The product was passed through a short column of alumina (4.2 × 4.0 cm). The fractions eluted with ether (900 ml) were collected and evaporated. The residue was chromatographed on alumina (3.6 × 8.0 cm). The fractions eluted with 40% hexane in benzene afforded a mixture of the *methanothia[27]annulene* (**13**) (123 mg, 5.2%). It formed dark purple needles, m.p. 201–203 °C (decomp.) (from THF–hexane);  $m/z$  382 ( $M^+$ , 65%) and 91 (100);  $M$ , 382.5; for UV data see Table 2 and Figure 6;  $\nu_{max}$  990, 970 ( $E-HC=CH$ ), and 740  $cm^{-1}$  ( $Z-HC=CH$ );  $\delta$  (500 MHz;  $CD_2Cl_2$ ) 7.54–6.80 (m, olefinic inner H), 6.50–5.80 (m, olefinic outer and 7-membered-ring H), 3.14 (s,  $CH_2$ ), and 3.06 (s,  $CH_2$ ) (see Figure 5) (Found: C, 84.6; H, 6.8.  $C_{27}H_{26}S$  requires C, 84.8; H, 6.85%).

**12,17-Methanothia[29]annulene (14).**—A solution of lithium ethoxide prepared from lithium (74.2 mg, 10.7 mmol) in dry ethanol (71 ml) was added dropwise during 3.5 h to a stirred solution of the salt (**4a**) (4.00 g, 5.37 mmol) and the dialdehyde (**3j**) (1.58 g, 4.13 mmol) in DMF (240 ml) at 65 °C. After being stirred for a further 30 min at 65 °C, the mixture was worked up as for the isolation of compound (**15**). The product was passed through a short column of alumina (4.2 × 4.0 cm). The fractions eluted with ether (400 ml) were collected and evaporated. The residue was chromatographed on alumina (3.2 × 7.0 cm). The fractions eluted with 40–70% ether in hexane afforded the *methanothia[29]annulene* (**14**) (70 mg, 4.1%). It formed dark red needles, m.p. 148–149 °C (from hexane–benzene);  $m/z$  408 ( $M^+$ , 13%) and 91 (100);  $M$ , 408.6; for UV data see Table 2;  $\nu_{max}$  990, 980 ( $E-HC=CH$ ) and 735  $cm^{-1}$  ( $Z-HC=CH$ );  $\delta$  (270 MHz) 7.22–5.76 (m, olefinic and 7-membered-ring H) and 2.64 (2 H, s,  $CH_2$ ) (see Figure 1) (Found:

C, 83.6; H, 8.4.  $C_{29}H_{28}S$  requires C, 85.2; H, 6.9%). Attempts to improve the elemental analysis failed.

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