

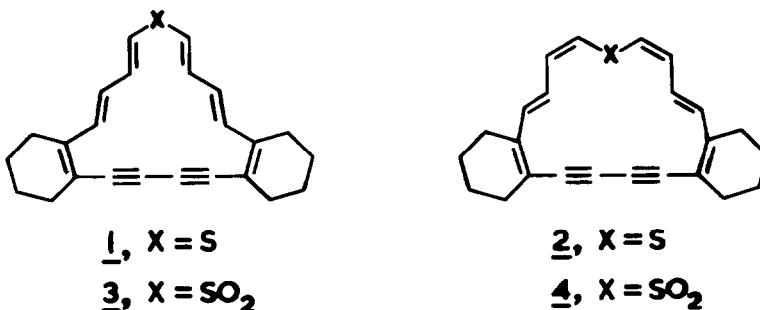
THE SYNTHESIS OF DIMETHYLBISDEHYDROTHIA[17]ANNULENES AND THEIR DIOXIDES,  
CONFIGURATIONAL AND CONFORMATIONAL ISOMERISM IN CONJUGATED 17-MEMBERED HETEROCYCLES <sup>1</sup>

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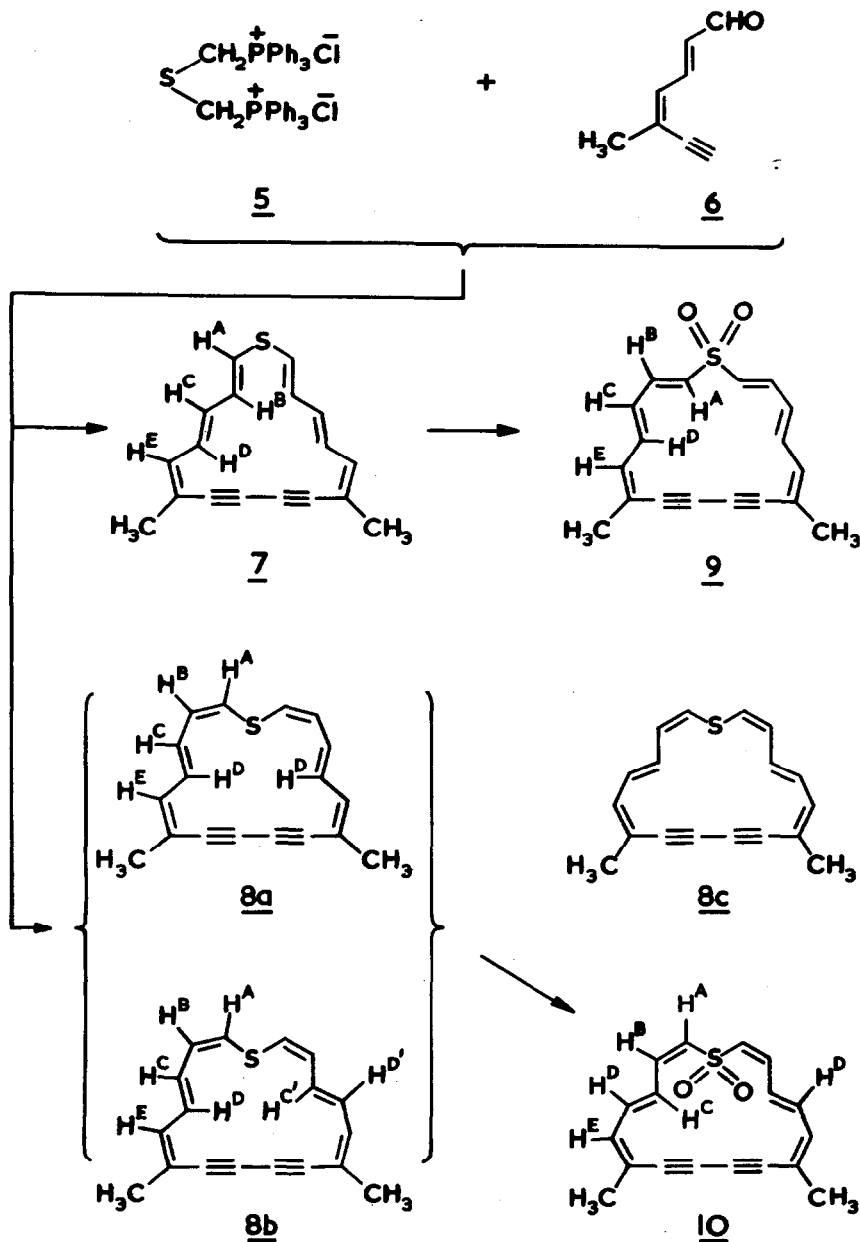
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The potentially diatropic ("aromatic") bis-cyclohexene annelated bisdehydrothia[17]-annulenes 1 and 2, as well as the potentially paratropic ("antiaromatic") sulphones 3 and 4, have been described previously.<sup>2,3</sup> Rather surprisingly, only the "all-trans" sulphide 1 appeared to be diatropic, whereas only the di-cis sulphone 4 was paratropic. We have since found that related 1,3-bisdehydroannulenes show conformational mobility,<sup>4,5</sup> and



that such mobility can obscure ring current effects. It was therefore decided to prepare the corresponding monocyclic dimethylbisdehydrothia[17]annulenes 7 and 8, as well as the sulphones 9 and 10, since ring currents and conformational mobility are more easily observed in the dimethyl than in the bis-cyclohexene annelated series. This work has shown that the previously reported<sup>2</sup> apparent anomaly was indeed due to conformational effects.

Treatment of 5<sup>6</sup> in ether with 2 mol equiv of  $n\text{-C}_4\text{H}_9\text{Li}$  at 20° gave the corresponding bis-ylid, which was allowed to react with 2 mol equiv of 6<sup>7,8</sup> at this temp for 2 hr. Chromatography on Al<sub>2</sub>O<sub>3</sub> (Woelm, act III) led to 42% of a stereoisomeric mixture of "acyclic sulphides", which was coupled directly with Cu(OAc)<sub>2</sub> in pyridine at 55° for ca 1 hr. Separation by short column chromatography<sup>9</sup> on Kieselgel (Merck GF<sub>254</sub>) gave the relatively stable dimethylbisdehydrothia[17]annulenes 7 and 8,<sup>10</sup> each of which was purified by chromatography on Al<sub>2</sub>O<sub>3</sub> (Woelm, act III). The "all-trans" isomer 7 (3.9% yield) formed red-orange needles;<sup>11</sup>  $m/e$  264;  $\lambda_{\text{max}}$  (ether) 253 ( $\epsilon$  9500), 268sh (11,700), 322 (39,700), 390sh nm (5300). The di-cis isomer 8 (5.6% yield) also formed red-orange needles;<sup>11</sup>  $m/e$  264;  $\lambda_{\text{max}}$  (ether) 244 ( $\epsilon$  13,000), 254 (17,200), 268 (17,200), ca 308sh (26,800), ca 323sh (41,100), 339 (47,500), ca 358sh (33,000), ca 408sh nm (5300).



Oxidation of **7** with excess *m*-chloroperbenzoic acid in  $\text{CH}_2\text{Cl}_2$  at  $0^\circ$  for 1 hr gave the sulfoxide **9** as yellow crystals;<sup>11,12</sup>  $\lambda_{\text{max}}$  (ether) 299 ( $\epsilon$  29,600), 374 nm (3300). Similar oxidation of **8** led to the sulfoxide **10** as red crystals;<sup>11,12</sup>  $\lambda_{\text{max}}$  (ether) 258 ( $\epsilon$  15,800), 271 (27,300), 286 (35,300), 295sh (31,600), 307 nm (32,800).

The  $^1\text{H}$ -nmr spectra of the dimethylbisdehydrothia[17]annulenes 7 and 8, and of the sulphones 9 and 10, are given in Table 1. The "all-trans" sulphide 7 is clearly diatropic, as the methyl protons resonate at relatively low field ( $-0.29$  ppm as compared with the "acyclic sulphides").<sup>13</sup> This is confirmed by the rather low field outer  $\text{H}^{\text{C}}$  and  $\text{H}^{\text{E}}$ , and high field inner  $\text{H}^{\text{D}}$  resonances. That both  $\text{H}^{\text{A}}$  and  $\text{H}^{\text{B}}$  in 7 resonate at high field, as in 1,<sup>2</sup> is undoubtedly due to the rotational mobility of these trans double bonds. Such mobility has already been established for the corresponding "all-trans" dimethylbisdehydrothia[13]annulene by low temperature  $^1\text{H}$ -nmr studies,<sup>5</sup> but cooling 7 to  $-100^\circ$  caused no significant change in the spectrum.

Table 1.  $^1\text{H}$ -Nmr Parameters of 7 - 10 at 100 MHz in  $\text{CDCl}_3$  ( $\tau$  Values; Internal Standard, TMS;  $\underline{J}$  Values in Hz in Parentheses)

Compd	$\text{H}^{\text{A}}$	$\text{H}^{\text{B}}$	$\text{H}^{\text{C}}$	$\text{H}^{\text{D}}$	$\text{H}^{\text{E}}$	$\text{CH}_3$
<u>7</u>	4.42d (15)	4.85dd (9,15)	3.09dd (9,15)	5.63qd (12,15)	2.81d (12)	7.78s
<u>8</u>	3.01d (9)	3.45dd (9,9)	3.61dd (9,15)	4.42dd (10,15)	3.11d (10)	7.78s
<u>9</u>	4.57d (15)	2.81dd (6,15)	3.37dd (6,15)	4.17dd (11,15)	3.10d (11)	7.90s
<u>10</u>	4.40d (11)	3.71dd (11,11)	-0.60dd (11,15)	ca 4.2 <u>a</u>	4.16 <u>b</u>	8.20s

a This signal could not be located precisely.

b Value obtained from dideuterio-10 (D instead of  $\text{H}^{\text{D}}$ ).

The  $^1\text{H}$ -nmr spectra of the di-cis sulphide 8 and sulphone 10 could only be interpreted through spectral examination of the corresponding dideuterio derivatives (8 and 10, D instead of  $\text{H}^{\text{D}}$ ,  $\text{H}^{\text{D}'}$ ), synthesised analogously from 5 and  $\beta$ -deuterio-6.<sup>8</sup> The di-cis sulphide 8 also appeared to be diatropic, as indicated by the low field position of the methyl proton resonance (Table 1). This was not clearly evident from the olefinic proton shifts, and it was suspected that conformational mobility was responsible. Indeed, cooling 8 ( $\text{THF-d}_8$ , 100 MHz) caused progressive broadening of the  $\text{H}^{\text{C}}$  and  $\text{H}^{\text{D}}$  signals, coalescence of each occurring at ca  $-30^\circ$ . Further cooling resulted in the appearance of new discrete high field bands. The spectrum at  $-75^\circ$  showed the presence of ca 45% of the symmetrical conformer 8a [ $\text{H}^{\text{D}}$ :  $\tau$  5.21dd ( $\underline{J} = 11.5, 16$  Hz)] and ca 55% of the unsymmetrical conformer 8b [ $\text{H}^{\text{D}}$ :  $\tau$  5.37dd ( $\underline{J} = 11.5, 16$  Hz);  $\text{H}^{\text{C}'}$ :  $\tau$  4.39dd ( $\underline{J} = 11.5, 13.5$  Hz)],<sup>14</sup> but none of the third possible conformer 8c. The presence of a symmetrical and the unsymmetrical conformer was confirmed by the three methyl proton singlets ( $\tau$  7.71, 7.75, 7.81) in the spectrum at  $-75^\circ$ . The outer olefinic protons in 8a and 8b at  $-75^\circ$  resonate in the region ca  $\tau$  2.3 - 3.5. The "frozen" spectrum confirms that 8 is diatropic, and undoubtedly the bis-cyclohexene annelated derivative 2<sup>2</sup> is also diatropic but conformationally mobile. The observation and interconversion of non-equivalent conformers has precedent in the carbocyclic dehydroannulene field,<sup>4,15</sup> but 8 is the first dehydroheteroannulene in which individual conformers could be detected by low temperature  $^1\text{H}$ -nmr spectrometry.

The "all-trans" sulphone 9 appears to exist mainly in the indicated conformation, as evidenced by the low  $\underline{J}_{\text{B,C}}$  value (6 Hz), and it exhibits no appreciable ring current. The  $^1\text{H}$ -nmr spectrum of the di-cis sulphone 10 points to the conformation shown (corresponding

to the absent 8c), in view of the relative chemical shifts of  $H^C$  and  $H^D$ . The sulphone 10 is clearly paratropic, as the inner  $H^C$  protons resonate at very low field, and the outer olefinic and methyl protons <sup>16</sup> at high field. The nmr spectra of both 9 and 10 were essentially temperature independent (9:  $-80^\circ$  to  $30^\circ$ ; 10:  $-100^\circ$  to  $100^\circ$ ). That the di-cis sulphone 10 is paratropic, but the "all-trans" sulphone 9 is atropic, parallels the observations already made with the annelated sulphones 3 and 4,<sup>2</sup> and indicates that the di-cis isomer can adopt a more planar conformation.

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8. The aldehyde 6 (or  $\beta$ -deuterio-6) was prepared most conveniently through homologation of cis-3-methyl-2-penten-4-ynal (or the corresponding CDO derivative)<sup>5</sup> by the method of T.M. Cresp, M.V. Sargent, and P. Vogel, *J. Chem. Soc. Perkin I* **37** (1974).
9. See B.J. Hunt and W. Rigby, *Chem. & Ind. (London)* 1868 (1967).
10. Attempts to prepare the corresponding oxygen analogs by a similar route were unsuccessful.
11. The compound decomposed on attempted melting point determination.
12. The molecular ion could not be observed in the mass spectrum, but the sulphone structure was confirmed by the presence of strong bands at ca 1130 and 1310  $\text{cm}^{-1}$  in the ir spectrum ( $\text{CHCl}_3$ ).
13. The corresponding methyl proton resonance difference in the atropic alcohol 7 (CHOH instead of S) is  $-0.04$  ppm, and in the paratropic ketone 7 (CO instead of S) it is  $+0.22$  (R.L. Wife, J. Ojima, and F. Sondheimer, unpublished experiments).
14. The assignments are based on the low-temperature  $^1\text{H}$ -nmr spectrum of dideuterio-8 (D instead of  $H^D$ ,  $H^{D'}$ ), and the relative proportions of 8a and 8b are derived by integration.
15. I.C. Calder, Y. Gaoni, P.J. Garratt, and F. Sondheimer, *J. Amer. Chem. Soc.* **90**, 4954 (1968).
16. The upfield shift of the methyl proton resonances in the  $^1\text{H}$ -nmr spectrum of 10 is  $+0.18$  ppm as compared to the corresponding "acyclic sulphones" (isomeric mixture), prepared by oxidation of the "acyclic sulphides" with m-chloroperbenzoic acid.