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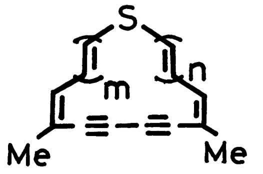
Synthesis and Properties of Methano-Bridged Thia[15]-, Thia[17]-, and Thia[19]annulenes

Shigeyasu KURODA, Yoshihiko NOZAWA, Yoshiharu YONEYAMA, Satoshi FUJITA,† Kazuhiro YANAGIHARA,† and Jūro OJIMA†*
Department of Industrial Chemistry, Faculty of Engineering, Toyama University, Gofuku, Toyama 930
†Department of Chemistry, Faculty of Science, Toyama University, Gofuku, Toyama 930

Title annulenes have been synthesized through a double Wittig reaction between the vinylogous dicarbaldehydes of 1,6-diformylcycloheptatriene and bis[(triphenylphosphonio)methyl]sulfide dibromide, and their ^{1}H NMR spectra were examined proving that the thia[17]- and -[19]annulenes sustain ring current, while the thia[15]annulene does not.

A variety of monocyclic and annelated thiaannulenes have so far been prepared.1) The known examples of many-membered ring compounds showing ring current effect are the bisdehydrothia[13]- (**1**: m=n=1), -[15]- (**1**: m=1, n=2), and -[17]annulene (**1**: m=n=2) as well as their cyclohexene-annelated and methano-bridged derivatives, prepared by Sondheimer et al.2) The methano-bridged thia[11]annulene **2** has also been prepared by a double Wittig reaction between 1,6-diformylcycloheptatriene (**3a**: m=n=0)3) and bis[(triphenylphosphonio)methyl]sulfide dibromide **4**,4) and has been shown to be atropic, due to severe deviation of the annulene perimeter from coplanarity, by Vogel et al.5)

Since the vinylogous dicarbaldehydes of **3a** were available to us,6) the double Wittig reaction used to obtain **2** has been applied to the synthesis of the higher homologs of **2**. It was expected that the desired higher-membered thiaannulenes show ring current effect beyond the size of the known thia[17]annulene,1) since a methano-bridge should contribute to keep the annulene perimeter coplanar, if the ring size is sufficiently large to release the steric strain caused by the introduction of the methano-bridge. This synthetic objective has now been verified in practice. In this paper, we describe synthesis and properties of the methano-bridged thia[19]annulene 7 as well as its smaller congeners 5 and 6.



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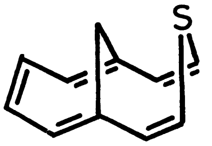

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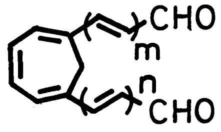
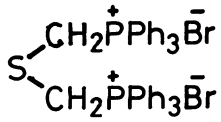


3a: m=n=0
3b: m=1 n=0
3c: m=n=1
3d: m=2 n=1
3e: m=n=2



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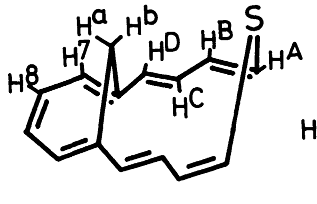

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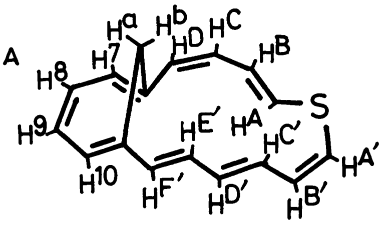

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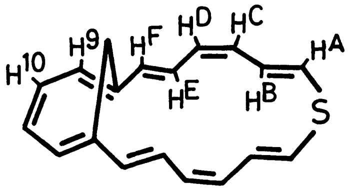

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The Wittig reactions of the dicarbaldehydes 3c–e[7)] and 4 with ethanolic lithium ethoxide in DMF at 80 °C afforded the desired monomeric thiaannulenes 5–7 in 1–2% yields, respectively; 6,11-methanothia[15]annulene 5[8,9)] [yellow needles, mp 110–111 °C, ^{1}H NMR (270 MHz in $CDCl_3$) δ=7.09–7.06 (m, H^8), 6.86 (dd, J=10.7, 8.3 Hz, H^B), 6.75 (br. s, H^7), 6.67 (d, J=16.1 Hz, H^D), 6.47 (dd, J=16.1, 10.7 Hz, H^C), 5.66 (d, J=8.3 Hz, H^A), 2.65 (d, J=12.5 Hz, H^b), 0.19 (d, J=12.5 Hz, H^a)]; 6,11-methanothia[17]annulene 6 [red needles, mp 120–121 °C, ^{1}H NMR (270 MHz in $CDCl_3$) δ=7.03–6.89 (m, H^7, H^8, H^9, H^{10}, $H^{D'}$), 6.76–6.65 (m, $H^{F'}$, H^D, $H^{B'}$), 6.49–6.42 (m, H^B, $H^{A'}$), 6.26 (dd, J=10.2, 4.8 Hz, H^C), 5.63 (dd, J=15.2, 11.3 Hz, $H^{C'}$), 5.11 (dd, J=15.4, 11.4 Hz, $H^{E'}$), 4.50 (d, J=16.1 Hz, H^A), 2.39 (d, J=13.2 Hz, H^b), 0.66 (d, J=13.2 Hz, H^a)]; 8,13-methanothia[19]annulene 7 [dark red needles, mp 127–128 °C, ^{1}H NMR (270 MHz in $CDCl_3$) δ=8.39 (dd, J=15, 9.5 Hz, H^E), 8.08 (dd, J=15, 10.5 Hz, H^B), 6.41–6.38 (m, H^{10}), 6.19 (d, J=15 Hz, H^A), 6.13–6.11 (m, H^9), 5.95 (d, J=15 Hz, H^F), 5.91 (t, J=10.5 Hz, H^C), 5.84 (t, J=10 Hz, H^D), 3.47 (s,

$-CH_2-$)]. These assignments were made on the basis of multiplicities and coupling constants, and were assisted by decoupling experiments.

In agreement with a prediction from molecular models, it is noteworthy that the methanothia[15]- **5** and -[17]annulene **6** were formed by these Wittig reactions, while the closely related carbocyclic methano[14]- and -[16]annulenes were not formed by intramolecular reductive couplings of the dicarbaldehydes **3d** and **3e**, respectively.$^{6)}$ In the formation of the methanothia[19]annulene **7**, a configurational change of the double bond occurred during the reaction. A similar change has been observed in formation of bisdehydro[15]annulenones and tribenz[14]-annulenes.$^{10)}$

Examination of the chemical shifts indicates that the thia[17]annulene **6** is diatropic, as might be expected for a 18π-electron system. This follows from the fact that the annulene outer protons in **6** resonate at low field, whereas the annulene inner protons including methylene protons at high field. On the other hand, the thia[19]annulene **7** is paratropic, as might be expected for a 20π-electron system. This follows from the fact that the annulene outer protons in **7** resonate at high field, whereas the annulene inner protons including methylene protons at low field. In contrast, the thia[15]annulene **5** is atropic, since both the annulene inner and outer protons in **5** resonate at almost the same field.

An inspection of molecualr models reveals that the coplanar annulene perimeters can be constructed more readily in the molecular models corresponding to the structures of **6** and **7**, as compared with that for **5**, which can be done only with difficulty. This is in accord with the consideration of ring current effect in **5**–**7**. From the ^{1}H NMR spectral data, it turns out that the thiaannulenes **5**–**7** exist in the conformations indicated. The 90 MHz ^{1}H NMR spectra of **5**–**7** were essentially temperature-independent over the range from -60 to 60 °C, thus ruling out any conformational change of **5**–**7** in this temperature range.

In the monocyclic annulene series, it is usually recognized that a tropicity in both [4n+2]π- and [4n]π-electron systems becomes less as the ring size increases.$^{11)}$ However, in the methano-bridged thiaannulene series **5**–**7**, the lower-membered [15]annulene **5** is atropic, while the higher-membered [17]- **6** and [19]-annulene **7** are diatropic and paratropic, respectively. As visualized by molecular model inspection, the methano-bridge of **5** would cause severe steric strain in a forced planar annulene ring structure. Namely, the 15-membered ring including a sulfur atom is not sufficiently large to relieve the strain. Thus, non-planarity of the annulene perimeter similar to that of **2** is responsible for the lack of tropicity of **5**. In the higher-membered rings **6** and **7**, the 1,6-methano-bridge serves to keep their annulene perimeters coplanar.

Further studies on methano-bridged thiaannulenes are now in progress.

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7) Under these conditions, **3b** did not afford the desired product.

8) Satisfactory elemental analyses were obtained for **5**–**7**.

9) Along with **5**, we could isolate the dimeric dithia[30]annulene. The details will be reported elsewhere.

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