

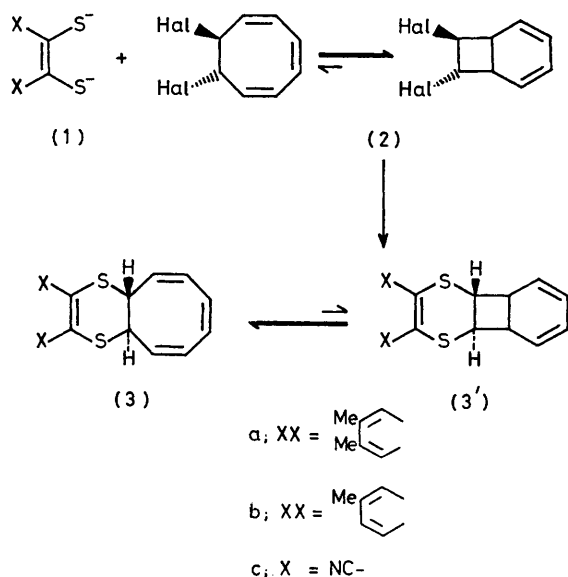
9,12-Dithia-*trans*-bicyclo[6.4.0]dodeca-2,4,6,10-tetraene System, an Example of a *trans*-Fused Cyclo-octa-1,3,5-triene

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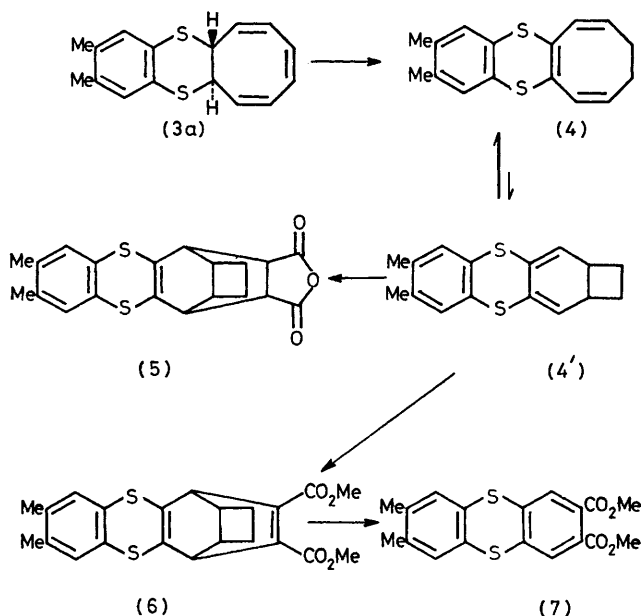
Summary Reaction of the 1,2-dithiols (**1a-c**) with cyclo-octatetraene *trans*-dihalides led to derivatives (**3a-c**) of the title system, whose special steric features permit synthetically useful transformations; thus thermal rearrangement gave the 3,4-fused 1,4-dithiinocyclo-octa-1,3,5-triene (**4**), base-induced isomerisation gave the 1,4-dithia[12]annulene (**8**), BF_3 -catalysed rearrangement gave the 2-benzyl-1,3-dithiole (**11**), and dehydrogenation gave the 1,4-dithiinocyclo-octatetraene (**12**).

In connection with our previous work¹ on novel sulphur heterocycles we were interested in the 9,12-dithia-*trans*-bicyclo[6.4.0]dodeca-2,4,6,10-tetraene system (**3**). Derivatives of (**3**) were obtained by reaction of cyclo-octatetraene *trans*-dihalides (**2**) with alkali metal salts of 1,2-dithiols (**1**), e.g., *o*-xylene-4,5-dithiol (**1a**), toluene-3,4-dithiol (**1b**), and



dimercaptomaleonitrile (**1c**), which gave, respectively, (**3a**) (68%, m.p. 163 °C), (**3b**) (35%, m.p. 88 °C), and (**3c**) (61%, m.p. 165 °C).[†] The mass spectra of (**3a-c**) showed loss of benzene due to the valence isomerisation (**3**) \rightarrow (**3'**); however, ¹H n.m.r. spectroscopy indicated that the compounds existed exclusively in the cyclo-octatriene form (**3**).[‡] The preference of structure (**3**) over (**3'**) is attributed to the strain that would be imposed by *trans*-fusion of the four-membered ring. This exceptional steric situation also governs the chemical behaviour of compounds (**3**) and we describe some unusual reactions of the benzo-derivative (**3a**).

Compound (**3a**) reacted with maleic anhydride and dimethyl acetylenedicarboxylate under relatively vigorous conditions (6 h in boiling toluene) to afford high yields of adducts having m.p.s 348 and 208 °C, respectively. The latter smoothly decomposed at 220 °C to a mixture of cyclobutene and the thianthrene (**7**) (85%, m.p. 116 °C).



This fragmentation indicated that the compound must have structure (**6**); the adduct with maleic anhydride is similarly formulated as (**5**). The Diels-Alder products thus are not derived from the valence tautomer (**3'a**) but are formed from the precursor (**4**) or (**4'**), which in turn arises from (**3a**) by two successive [1,5]-sigmatropic hydrogen shifts. Indeed, compound (**4**) (m.p. 130 °C) was isolated in 78% yield when (**3a**) was boiled in xylene. Its ¹H n.m.r. spectrum [$\delta(\text{C}_6\text{D}_6)$ 6.89 (s, 2H), 5.91 (d, 2H, *J* 12 Hz), 5.62 (m, 2H), 2.03 (t, 4H), and 1.78 (s, 6H)] gives no indication of the presence of the isomer (**4'**). The Diels-Alder reactions of (**4**), leading to (**5**) and (**6**), occurred under much milder conditions (0.5–1 h in boiling benzene) than with (**3a**).

Treatment of (**3a**) with $\text{KOBu}^t\text{-Me}_2\text{SO}$ at 40 °C gave an isomer (20%, m.p. 143 °C), which is assigned the structure (**8**). The mass spectrum indicated two fragmentation paths, one *via* the annulene² (**9**) by loss of two molecules of acetylene and the other *via* (**3a**) by recyclisation. The ¹H n.m.r. spectrum (CS_2) of (**8**) showed only signals due to

[†] Satisfactory analytical results were obtained for all new compounds.

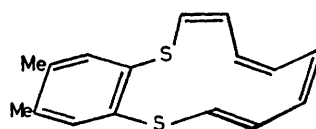
[‡] E.g. for (**3a**): $\delta(\text{CCl}_4)$ 7.00 (s, 2H), 5.95 (s, 6H), 4.19 (s, 2H), and 2.05 (s, 6H).

eight olefinic protons, centred at δ 5.67, besides those due to the aromatic and the methyl protons. The spectrum is temperature-dependent (-80 – 0 °C), pointing to conformational lability of the molecule. The appearance of two close singlets due to the methyl protons is in best accord with the *trans,cis,cis,cis*-configuration (8). The chemical shifts of the olefinic protons, as well as the u.v. spectrum [λ_{\max} (dioxan) 230 nm ($\log \epsilon$ 4.70), 253 (4.40), and 302 (3.82)], rule out any aromatic character in the heterocyclic unit, although it is formally a 14π -system.

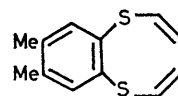
Compound (8) is evidently produced from (3a) by way of its anion [confirmed by H-D exchange in $(\text{CD}_3)_2\text{SO}$ in the presence of KOBU^{\dagger}] and reprotonation to the *cis*-isomer, which then undergoes spontaneous conrotatory ring-opening. The reluctance of (3a) to undergo the electrocyclic reaction may be attributed to the clamping effect of the *trans*-connecting S-C=C-S bridge, which would impose considerable strain on the transition state of the conrotatory process. In the absence of this link ring-opening occurs easily, as demonstrated by the reaction of (2) with sodium thiophenolate to give (10) (11%, m.p. 154–156 °C).§

In contrast to the behaviour of (3a) towards base, reaction with $\text{BF}_3\text{-Et}_2\text{O}$ resulted in a skeletal rearrangement to give (11) [57%, m.p. 123 °C, δ (C_6D_6) 7.02–6.78 (m, 5H), 6.70 (s, 2H), 4.60 (t, 1H), 2.91 (d, 2H, J 8 Hz), and 1.76 (s, 6H), m/e 272 (M^+), 195 ($M^+ - \text{C}_6\text{H}_5$), and 181 ($M^+ - \text{C}_7\text{H}_7$)]. This rearrangement has analogies in the chemistry of monocyclic cyclo-octatrienes.³

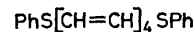
Dehydrogenation of (3a) with dichlorodicyanobenzoquinone in boiling benzene gave (12) [78%, m.p. 170 °C, m/e 270 (M^+), λ_{\max} (dioxan) 292 nm ($\log \epsilon$ 4.11), and 344



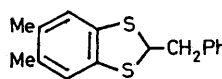
(8)



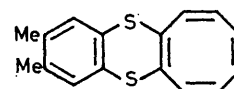
(9)



(10)



(11)



(12)

(3.52)]; the isomeric cyclo-octatriene (4a) did not react under these conditions. The contrasting behaviour of the two isomers is a further indication of the inherent strain in the former, which provides a driving force for the dehydrogenation. The ^1H n.m.r. spectrum of the annelated cyclo-octatetraene (12) exhibits signals due to six olefinic protons, centred at δ 5.80; there is no evidence for the existence of electrocyclic valence isomers at room temperature.

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§ Compound (10) showed δ (CS_2) 7.18 (br s, 10H) and 6.23, 6.08 (m, 8H); the configurational assignment is not certain.

¹ E.g.: W. Schroth, F. Billig, and G. Reinhold, *Angew. Chem. Internat. Edn.*, 1967, **6**, 698; W. Schroth, F. Billig, and A. Zschunke, *Z. Chem.*, 1969, **9**, 185, and references cited therein.

² W. Schroth and L. Moegel, *Z. Chem.*, 1977, **17**, in the press.

³ E.g.: C. R. Ganellin and R. Pettit, *J. Chem. Soc.*, 1958, 576.