X-Ray Crystal Structure of 13,14,15-Trithiapentacyclo[9.5.1.$1^{3,9}$.$0^{4,8}$.$0^{12,16}$]-octadec-5-ene

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Summary The structure of the title compound, $C_{15}H_{18}S_3$, a tricyclopentadiene derivative, has been determined by *X*-ray crystallography and shown to contain an *exo*-trithiolan ring; the configuration of the bisnorbornyl species is revealed to be *endo-exo-endo.*

exo- and *endo*-DICYCLOPENTADIENES react with amine-activated sulphur to form compounds of formula $C_{10}H_{12}S_3$ believed to have structures incorporating *exo*-orientated trithiolan rings.[1] Although crystalline, neither of these derivatives was suitable for *X*-ray crystallography.

Tricyclopentadiene, under similar conditions, also acquires three sulphur atoms to form $C_{15}H_{18}S_3$. Crystals of this, which were grown from $CHCl_3$ solution, were suitable for structural analysis. An added bonus from such a determination on this compound was that the orientation of the organic part of the molecule could be settled.

Originally tricyclopentadiene, synthesised from C_5H_6, was assumed to be a mixture of two of the possible eight stereoisomers; these were (*exo-exo*)*-exo* and (*exo–exo*)*–endo*.[2] It was later reasoned that the configurations of the two norbornyl rings should be (*endo–exo*)[3] and the two stereoisomers were (*endo–exo*)*–exo* and (*endo–exo*)*–endo*, the latter being the predominant isomer. This compound is a white crystalline solid, m.p. 68 °C. No structural determination has been performed on it, or indeed on any of these multiply bridged systems. Support for the (*endo–exo*) configuration, however, has been proposed from ^1H n.m.r. data.[4]

The structure of $C_{15}H_{18}S_3$ shows the molecule to have the *exo–*(*endo–exo*)*–endo* configuration (Figure) confirming both the trithiolan structure and that proposed for the chief tricyclopentadiene isomer.[3,4]

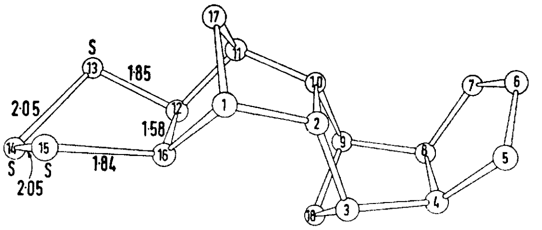

FIGURE. Structure of the title compound, *exo–*(*endo–exo*)*–endo*-$C_{15}H_{18}S_3$.

The yellow crystals of $C_{15}H_{18}S_3$, m.p. 189 °C, are monoclinic, space group $P2_1/n$ (uniquely determined from systematic absences), $a = 12{\cdot}025(12)$; $b = 14{\cdot}349(15)$; $c = 8{\cdot}460(4)$ Å; $\beta = 112{\cdot}06(57)°$; $U = 1353$ Å^3; $Z = 4$; $D_c = 1{\cdot}443$ g cm^{-3}. Intensity data were collected to a maximum θ of 65° using a Siemens off-line 4-circle diffractometer. Of the 2008 reflections thus measured 105 were classified as unobserved.[5] The data were processed in the usual way[6] and the structure was solved by direct methods. The *R* factor, before inclusion of any hydrogen atoms, and with all S and C atoms refining anisotropically, is 0·076, but the data have not yet been corrected for absorption. In view of the significant amount of refinement still to be done, full details of bond lengths and angles are not given here but the parameters of the trithiolan ring are shown in the Figure.†

The S–S bond lengths in the trithiolan ring are the same as those of the linear dialkyl trisulphides: $(CH_3)_2S_3$, 2·04;[7] $(CF_3)_2S_3$, 2·07;[8] $(ICH_2CH_2)_2S_3$, 2·05;[9] and $(CCl_3)_2S_3$, 2·03 and 2·04 Å.[10] Clearly the reduced reactivity of the trithiolan sulphur atoms over their linear counterparts is not due to any difference in bond character.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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