X-Ray Crystal Structure of 1,5-Dibromotetracyclo[4.2.2.$2^{2,5}$$0^{2,6}$]dodecane

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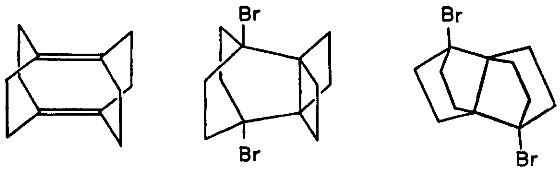
Summary The reaction of tricyclo[4.2.2.$2^{2,5}$]dodeca-1,5-diene with bromine gives a novel saturated dibromide with a 1,5-bridge, as determined by *X*-ray crystallography.

The reaction of tricyclo[4.2.2.$2^{2,5}$]dodeca-1,5-diene (**1**) with bromine gave a dibromide with no olefinic carbons, as indicated by its ^{13}C n.m.r. spectrum.[1] The symmetry required by the n.m.r. spectrum allows only two structures for the dibromide, (**2**) or (**3**).



(1) (2) (3)

These compounds would be formed *via* a transannular interaction between one of the double bonds and a developing cationic centre. In the case of 1,5-cyclo-octadiene, a corresponding reaction occurred, which involved a 1,5-bridge.[2] If compound (**1**) reacted in the same fashion it would give (**3**). On the other hand, a bridged 1,5-cyclo-octadiene in which the double bonds are rigidly held facing each other was found to give predominantly a 1,4-bridge.[3] The fusion of two norbornane units along a common 1,7-bond would lead to considerable distortion of the rings, and a 1,5-bridge would require marked twisting of compound (**1**) during the reaction. Thus, (**2**) would be a reasonable structure for the product. Since neither the spectroscopic data nor precedent allowed us to distinguish between the two structures, the substance was examined by *X*-ray crystallography.

Crystal data: $C_{12}H_{16}Br_2$, triclinic, space group $P\bar{1}$, $a = 6{\cdot}609(2)$, $b = 7{\cdot}318(2)$, $c = 7{\cdot}485(2)$ Å, $\alpha = 69{\cdot}98(2)$, $\beta = 62{\cdot}24(2)$, $\gamma = 64{\cdot}72(2)°$, $Z = 1$. Diffraction data were collected using an Enraf–Nonius CAD-4 diffractometer; 890 reflections ($\theta \leqslant 26°$) [$F^2 \geqslant 3{\cdot}0\ \sigma(F^2)$] were used in the structure solution and refinement. The structure was solved by a combination of Patterson and difference-Fourier techniques and refined by full-matrix least-squares methods. All programs were those of the Enraf–Nonius SDP program library. Final values of the residuals were R 0·042 and R_W 0·053.†

Crystallographically, the molecule contains a centre of symmetry. Its molecular structure is shown in the Figure. All hydrogen atoms were located and refined and were found to have normal bond lengths and angles. The torsional angle formed by C(1)–C(4)–C(1′)–C(4′) is 0·0° which indicates that the two norbornyl rings were not twisted. The C(1)–C(4)–C(4′) angle is close to that in norbornane,[4] but the external C(1)–C(4)–C(5′) angle is 123·7°, considerably larger than normal. This is the same as that recently observed by Gassman and Hoye[5] for another polycyclic compound which has an unusually large C–C–C bond angle, but considerably smaller than we have previously observed for tricyclo[4.2.0.0^{1,4}]octane (132·5°).[6]

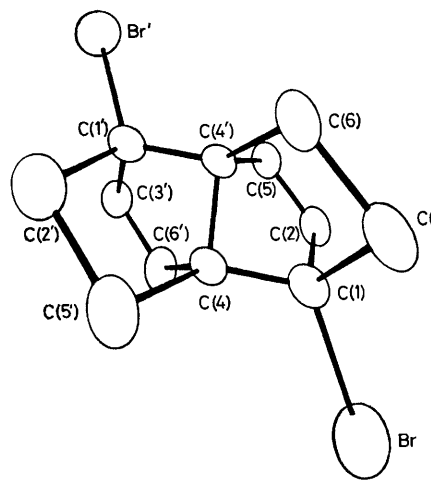


FIGURE. A perspective ORTEP[7] drawing of the dibromide (**3**). The principal structural parameters are as follows: bond lengths, Br–C(1) 1·963(3), C(1)–C(2) 1·550(4), C(1)–C(3) 1·535(4), C(1)–C(4) 1·502(4), C(2)–C(5) 1·570(5), C(3)–C(6) 1·567(5), C(4)–C(4′) 1·570(6), C(4′)–C(5) 1·555(4), C(4′)–C(6) 1·564(4) Å; bond angles, C(1)–C(2)–C(5) 102·0(2), C(1)–C(3)–C(6) 102·5(2), C(1)–C(4)–C(4′) 93·4(3), C(1)–C(4)–C(5′) 123·7(2), C(2)–C(1)–C(3) 107·4(3), C(2)–C(1)–C(4) 104·0(2), C(4)–C(4′)–C(5) 102·5(3), C(4)–C(4′)–C(6) 101·5(3), C(5)–C(4′)–C(6) 106·0(2), Br–C(1)–C(2) 111·9(2), Br–C(1)–C(3) 112·5(2), Br–C(1)–C(4) 116·2(2)°; and torsion angles, C(1)–C(4)–C(4′)–C(1′) 0·0, C(1)–C(2)–C(5)–C(4′) 0·0, C(1)–C(3)–C(6)–C(4′) 0·0°.

The reaction of (**1**) with bromine has thus been found to give (**3**) as the product. This reaction provides a convenient entry into a previously unknown ring system. Calculations which deal with the energies of these compounds and the course of the reaction will be reported elsewhere.

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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 Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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