A Stereospecific Dimerization of Norbornadiene Derivatives and the Crystal Structure of Heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecane†

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A molybdenum-mediated dimerization of norbornadiene and its 7-t-butoxy derivative gives good yields of products with a cage skeleton, heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecane, whose structure has been analysed by *X*-ray crystallography.

Metal-assisted dimerization of norbornadiene (NBD) was first observed in 1961[1] and since then has been studied extensively.[2] An ordinary dimerization of NBD generally produces several isomers simultaneously.[3] Only a few stereospecific reactions have been reported.[4] Recently we have observed a stereospecific *endo–cis–endo* coupling of NBD in the presence of hexacarbonylmolybdenum.[5] The cage molecule heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecane (**1**) is formed exclusively in a yield of 26%.

In this report the study of the dimerization is extended to the 7-t-butoxy derivative of norbornadiene (BNBD). The presence of an oxygen atom on the *exo*-face of BNBD might enhance *exo*-complexation to the metal and therefore reduce the degree of stereoselectivity of *endo–endo* coupling,[6] but our results showed negligible interference. In a typical experiment, BNBD (3 equiv.) and $Mo(CO)_6$ (1 equiv.) were refluxed in petroleum (110—140 °C) for 90 h. Compound (**2**) was isolated by column chromatography and was recrystallized from methanol to give a 40% yield of a white, waxy solid, m.p. 124—125 °C (lit.,[7] 131—132 °C). Spectroscopic data (^{1}H n.m.r., i.r., mass spectrometry) are identical to the reported values. The stereoselectivity was very high since no other isomers were found. Thus this reaction has provided a practical way for making these interesting cage molecules with and without a substituent on the methylene carbon.

Both the structures of (**1**) and (**2**) consist of eight five-membered rings. The rigid, highly symmetrical D_{2d} framework of (**1**) has drawn wide interest since its discovery. *X*-Ray structure analysis has been completed for (**2**),[8] yet the work for (**1**) was not successful. The problem arose because of serious crystal twinning which had been recognized by several investigators.[1,9] Aided by the high yield of the present method, we are able to produce (**1**) in larger quantity and consequently grow crystals in sizes suitable for *X*-ray analysis. The crystals were grown in a small flask from a diethyl

Table 1. Comparison of bond lengths.

	Carbon no.			
	1–2	1–8	7–8	1–14
(**1**)[a]	1.561(2)	1.532(6)	1.523(3)	1.531(7)
(**2**)[b]	1.568(4)	1.537(4)	1.530(3)	1.535(4)
Norbornane[c]	1.578(18)	1.534—1.535(14—35)[d]		

[a] The chemically equivalent bonds are averaged and the standard deviations are calculated by the equation: $[\Sigma(X_j - \bar{X})^2/(n - 1)]^{\frac{1}{2}}$. [b] Single crystal *X*-ray data quoted from ref. 8. [c] Electron diffraction data quoted from ref. 8. [d] Bond lengths of C(1)–C(8) and C(7)–C(8) are within similar ranges.

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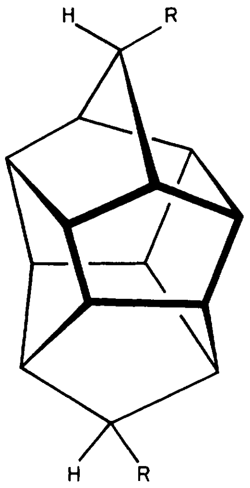
† The title compound, 1,3,4,6-ethanediylideneperhydrodicyclopenta[*cd,gh*]pentalene, has also been named as heptacyclo[5.5.1.1^{4,10}.0^{2,6}.0^{3,11}.0^{5,9}.0^{8,12}]tetradecane[1] or heptacyclo[9.3.0.0^{2,6}.0^{3,10}.0^{4,8}.0^{7,14}.0^{9,13}]tetradecane,[10] and may be abbreviated as 'cyclo-octaquinane'. For systematic nomenclature of polycyclic organic compounds, see D. van Binnendky and A. C. Mackay, *Can. J. Chem.*, 1973, **51**, 718.

Table 2. Comparison of bond angles.

	Carbon no.					
	1–8–7	1–8–9	6–7–8	2–1–8	2–1–14	8–1–14
(**1**)[a]	104.2(2)	100.1(3)	94.6(1)	103.0(6)	104.9(3)	107.9(2)
(**2**)[b]	103.8(4)	100.4(2)	95.1(1)	103.0(2)	105.0(2)	107.5(2)
Norbornane[c]	101.8	107.1	95.2	103.0		

See Table 1 for footnotes.



(**1**) R = H
(**2**) R = OBu^t

ether–methanol solution. A single crystal, ground to a suitable spherical size, was sealed in a lithium glass capillary for the X-ray diffraction study.

Crystal data: monoclinic, space group $P2_1/c$, $a = 8.744(2)$, $b = 7.605(2)$, $c = 14.136(3)$ Å, $\beta = 92.42(2)°$. Intensity data were measured on a CAD-4 automated diffractometer with monochromatized Mo-K_α radiation. Scanned with a variable-speed ω–2θ method, the data were collected up to $2\theta = 65°$. The structure was solved by MULTAN and refined by least-squares. Out of 3402 unique reflections measured, 2197 with $I > 3\sigma(I)$ (counting) were used in the analysis. Final R and R_ω were 0.051 and 0.033 respectively for counting statistical weights. Carbon atoms were treated anisotropically and hydrogen atoms isotropically. Absorption corrections were applied.‡

An ORTEP drawing of compound (**1**) is shown in Figure 1. The chemically equivalent structure parameters are averaged and listed in Tables 1 and 2, together with those for compound (**2**) and norbornane for comparison. Bond lengths and angles of (**1**) and (**2**) are consistent with each other and very close to the corresponding values for norbornane. The newly formed bonds have an averaged length of 1.531 Å and the two new angles have values of 104.9 and 107.9°. These values indicate a relatively low-strain geometry. Once the two norbornadiene moieties are held by the metal, cyclization with the formation of four five-membered rings [such as in (**1**) and (**2**)] should proceed more easily than the formation of two four-and-six-membered rings [another mode of *endo–cis–endo* coupling with a 90° twist with respect to the formation of (**1**)].

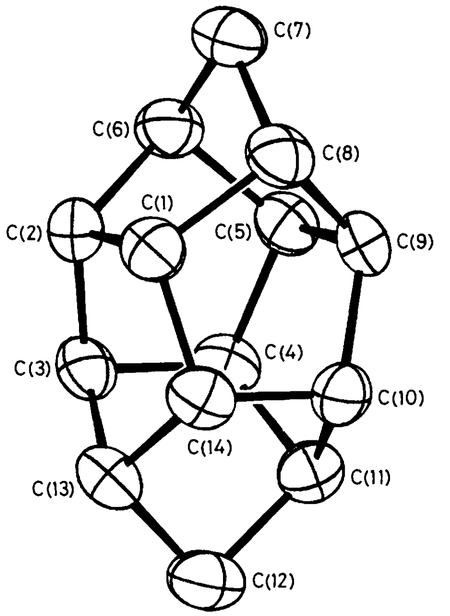


Figure 1. ORTEP drawing of compound (**1**).

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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.