Hexacyclo[10,3,1,$0^{2,10}$,$0^{3,7}$,$0^{6,15}$,$0^{9,14}$]hexadecane; an Ethanocongressane

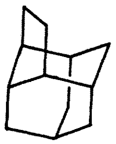
By S. T. Rao and M. Sundaralingam*
(*Department of Biochemistry, University of Wisconsin, Madison, Wisconsin* 53706)
and E. Osawa, E. Wiskott, and P. von R. Schleyer
(*Department of Chemistry, Princeton University, Princeton, New Jersey* 08540)

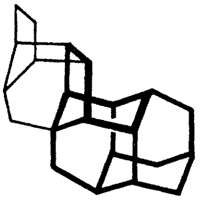
Summary The structure of a hydrocarbon, m.p. 110—111·5°, obtained from two different cyclo-octatetraene dimers (V) and (VI) by hydrogenation followed by aluminium halide rearrangement has been determined by *X*-ray analysis to be an ethanocongressane, hexacyclo[10,3,1,$0^{2,10}$,$0^{3,7}$,$0^{6,15}$,$0^{9,14}$]hexadecane (III).

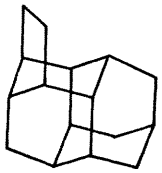
The regular diamondoid molecules, adamantane,[1] diamantane (congressane),[2] and triamantane[3] are readily available by aluminium halide rearrangement of isomeric polycyclic hydrocarbons. Other cage hydrocarbons of irregular structure can also be prepared by this method; examples include noradamantane,[4] ethanoadamantane {tetracyclo[6,3,1,$0^{2,6}$,$0^{5,10}$]dodecane (I)}, and "bastardane" (II).[6] We have obtained hexacyclo[10,3,1,$0^{2,10}$,$0^{3,7}$,$0^{6,15}$,$0^{9,14}$]hexadecane (III), one of the two isomeric ethano-bridged diamantanes (III and IV), by similar procedures.

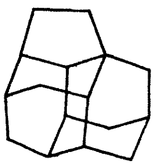
The third dimer of cyclo-octatetraene (V),[7] m.p. 40—41°, was exhaustively hydrogenated with a platinum catalyst until three moles of hydrogen were taken up and spectral evidence for the presence of the cyclopropane ring was absent. This product, $C_{16}H_{22}$, a mixture of at least two isomers as shown by g.l.c., was rearranged by treatment with $AlBr_3$-sludge catalyst[3–6] to give a solid product in good yield. Using preparative gas chromatography (Carbowax, 3/8 in × 25 ft) the product was separated into a major component (m.p. 206·5—208°, *ca.* 85%) and a minor one (m.p. 110—111·5°, *ca.* 15%). Both components were hexacyclic isomers, $C_{16}H_{22}$, and had remarkably similar mass spectra characterized by intense molecular-ion peaks at *m/e* 214. The n.m.r. spectra of both were complex but similar: it is likely that both isomers have similar structures.

Another route also gave the isomer with m.p. 110—111·5°. Hydrogenation of the fourth cyclo-octatetraene dimer (VI)[7] gave (VII), m.p. 38·5°, which was treated with the $AlBr_3$-sludge catalyst at 100°. The liquid product, separated by gas chromatography, consisted of an 80:20 mixture of a liquid $C_{16}H_{22}$, which proved to be identical with the isomer of m.p. 110—111·5° obtained from (V).


(I)

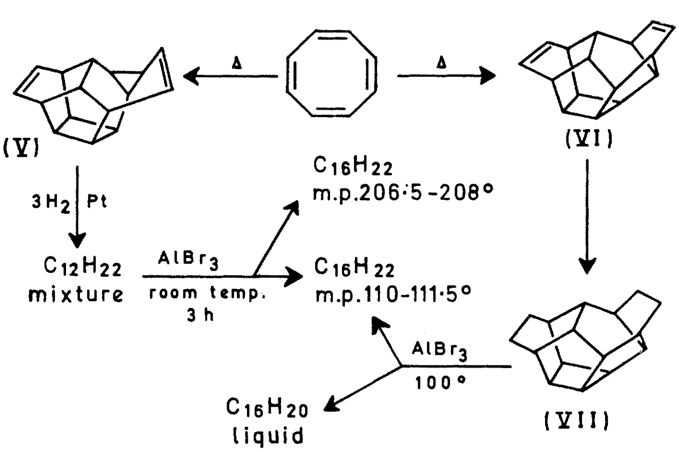

(II)


(III)


(IV)

On the basis of our experience in the synthesis of (I) by rearrangement, we suspected that the $C_{16}H_{22}$ isomers might be the ethano-bridged diamantanes, (III) and (IV). The higher melting material was unsuitable for *X*-ray analysis,[8] but the isomer with m.p. 110—111·5° gave good results. The structure was shown to be (III).

Crystals of (III) belong to the monoclinic space group $P2_1/c$ with $a = 9{\cdot}151 \pm 0{\cdot}001$, $b = 6{\cdot}510 \pm 0{\cdot}001$, $c = 19{\cdot}733 \pm 0{\cdot}003$ Å and $\beta = 98{\cdot}62 \pm 0{\cdot}02°$. $D_c = 1{\cdot}228$ g cm^{-3} ($Z = 4$) and $D_m = 1{\cdot}220$ g cm^{-3}. Using 1680 X-ray reflections recorded on a Picker four-angle diffractometer, the structure was solved by the straightforward application of the symbolic addition method.[9] Full-matrix least-squares refinement gave an agreement index of 0·044.



The C–C distances range from 1·516—1·552 Å with a mean of 1·534 Å. The C–C–C angles range from 99·9—114·5° with a mean of 109·1°. The largest variations in the bond angle are associated with C(7). The angle C(3)–C(7)–C(6) is compressed to 99·9° while the other two angles at C(7) are expanded to 114·5°. The cyclopentane ring is in the envelope form, the four atoms C(3), C(4), C(5), and C(6) being planar (see Figure).

In view of their similar mode of synthesis and spectroscopic properties, it is likely that both products from hydrogenated (V) are ethano-bridged diamantanes. Therefore, we suggest that the isomer with m.p. 206·5—208° may have structure (IV). This possibility is being checked by synthesis.

The ethano-bridged diamondoid molecules appear to be the most thermodynamically stable arrangements obtainable when two carbons and an additional ring are added to adamantane and to the higher adamantane analogues. Thus, (I) ($C_{12}H_{18}$) is a tetracyclic relative of adamantane ($C_{10}H_{16}$) and (III) and (IV) (both hexacyclic $C_{16}H_{22}$ isomers) are similarly related to diamantane ($C_{10}H_{26}$). (II) contains an ethanodiamantane (III) part-structure [shown in the structure of (II) by heavy lines].

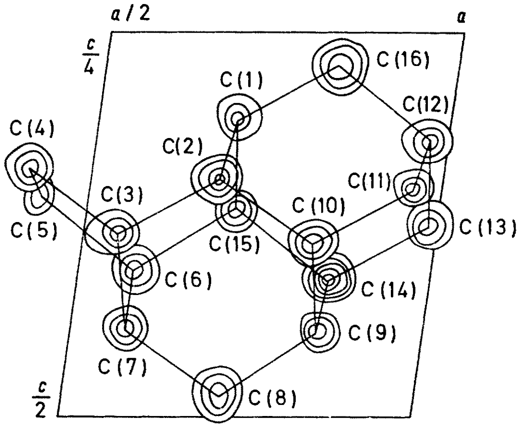


FIGURE. *The* E-*map of* (III) *showing the carbon skeleton*

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