Gas-phase Reactions on Platinum. Synthesis and Crystal Structure of *anti*-Tetramantane, a Large Diamondoid Fragment

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Summary *anti*-Tetramantane, a $C_{22}H_{28}$ hydrocarbon having the regular topology of the diamondoid lattice, has been synthesised by a double homologation of diamantane, the key step involving a ring expansion–cyclisation reaction of a polycyclic diene in hydrogen in the gas phase on a platinum–silica catalyst; the structure has been established by an *X*-ray crystal analysis.

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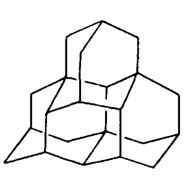
A multitude of structural isomers of $C_{22}H_{28}$ are possible, but only three possess the distinctive topology of the diamondoid lattice: iso-tetramantane, C_{3v}(**1**), *anti*-tetramantane, C_{2h}(**2**), and *skew*-tetramantane, C_2(**3**), so designated[1] to emphasise the close formal similarities between the fourth members of the diamondoid series and those of the aliphatic series, iso-butane and the two minimum energy conformations of n-butane, *anti* and *skew*.[2] None of the tetramantanes has been synthesised, an attempt[1] to produce one or more of the isomers by the Lewis acid rearrangement route,[3] successful for the lower members of the series, having failed. The elaboration of one member of the series into another represents an alternative approach to the larger diamondoid hydrocarbons and recently we showed that triamantane (**5**) could be synthesised from diamantane *via* an unusual gas-phase rearrangement of the intermediate olefin (**4**) in hydrogen on a platinum–silica catalyst.[4] A simultaneous double homologation of diamantane has now been realised leading to the first synthesis of a tetramantane isomer.

Exposure of diamantane to hot bromine produced the 1,6-dibromide (**6**)[5] which could be hydrolysed to the diol (**7**) in hot aqueous dimethylformamide. Koch–Haaf carboxylation[6] of the diol furnished the di-acid (**8**) and successive treatment of this substance with oxaloyl chloride in boiling benzene and ethereal diazomethane produced the crystalline bis-diazoketone (**9**) in good yield. Slow addition of (**9**) to a suspension of $CuSO_4$ in hot toluene yielded, after purification by chromatography, *ca.* 10% of a substance whose spectral and analytical data were consistent with di-ketone structures (**10**) and/or (**11**).[7] One or other of the isomers was acceptable for our purposes and although g.l.c. analysis revealed but one component, the product was almost certainly a mixture of the two; for convenience, the remaining intermediates are depicted as if they were derived from di-ketone (**10**) only. Prolonged exposure of the di-ketone to ethereal ethylmagnesium bromide produced the diol (**12**) which was readily dehydrated in hot benzene containing iodine, yielding the diene (**13**), also presumed to be a mixture of isomers.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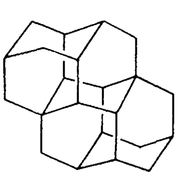
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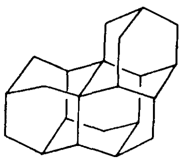
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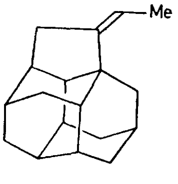

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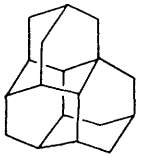
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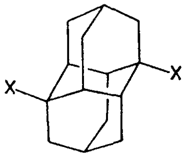
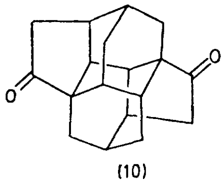


(6) X = Br
(7) X = OH
(8) X = CO_2H
(9) X = $COCHN_2$



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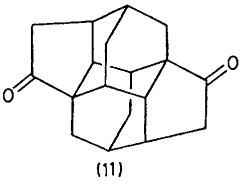

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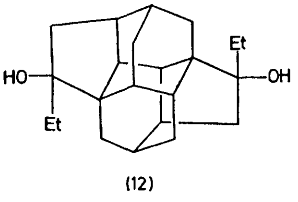

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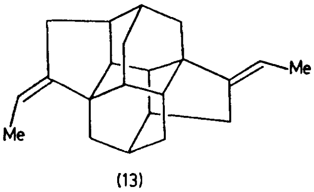

(13)

The final transformation was brought about in a flow system in which the diene (**13**) (100 mg) was vapourised in a stream of hydrogen and passed over a platinum on silica catalyst (*ca.* 10 g; 2% w/w in Pt) at 350—360 °C. The product was collected in a cold trap and recrystallised from acetone, yielding crystals (7·5 mg) of *anti*-tetramantane (**2**), m.p. 173·5—174·0 °C with a pre-melting transition at 159 °C. *X*-Ray diffraction was used to determine the structure. Crystals of (**2**) are monoclinic, space group $P2_1/n$, $a = 6{\cdot}495$, $b = 11{\cdot}558$, $c = 10{\cdot}330$ Å, $\beta = 98{\cdot}22°$. Three-dimensional intensity data were obtained using graphite-monochromated Mo-K_α radiation and a Hilger and Watts four-circle diffractometer. The structure (Figure) was solved by direct methods and has been refined by least-squares techniques with anisotropic thermal parameters for the carbon atoms. The hydrogen atoms were included with isotropic temperature factors in the refinement. The present value of R is 0·040 for 787 observed $[I > 3\sigma(I)]$ reflections. The molecule is constrained by space group requirements to be centrosymmetric. The carbon skeleton is a fragment of the diamond lattice with bond lengths ranging from 1·521(5) to 1·545(4) (mean 1·533) Å and valence angles ranging from 107·4 to 111·8 (mean 109·8) degrees. Full details of this analysis will be published elsewhere.[8]

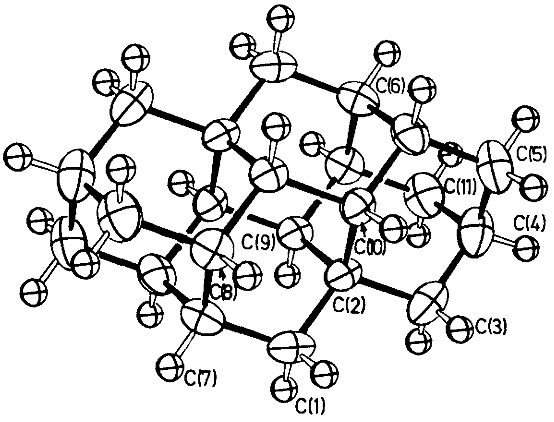

Figure. *X*-Ray structure of *anti*-tetramantane (**2**)

The mass spectrum of *anti*-tetramantane is consistent with a highly interlocking structure, resistant to fragmentation: the molecular ion peak at m/e 292 is by far the most prominent; of the remainder, only those at m/e 291 and 91 are of noticeable intensity, 30 and 13% respectively.‡ The i.r. spectrum is remarkably featureless, consistent with a structure of high symmetry Apart from the CH and CH_2 bond stretching absorptions centred at 2900 cm^{-1}, there are only six sharp absorptions of moderately weak intensity. The 90 MHz ^1H n.m.r. spectrum of *anti*-tetramantane exhibits a multiplicity (six separate resonances for seven different kinds of protons) in keeping with its structure.

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‡ The mass spectrum of triamantane exhibits similar features; see ref. **3** (c).

[1] P. v. R. Schleyer, E. Osawa, and M. G. B. Drew, *J. Amer. Chem. Soc.*, 1968, **90**, 5034.

[2] Molecular mechanics calculations indicate that the order of stability of the tetramantane isomers is iso > *anti* > skew; personal communication from Professor E. Osawa.

[3] (a) Adamantane: P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1957, **79**, 3292; (b) diamantane: C. A. Cupas, V. Z. Williams, jun., P. v. R. Schleyer, and D. J. Trecker, *ibid.*, 1965, **87**, 917; T. M. Gund, E. Osawa, V. Z. Williams, jun., and P. v. R. Schleyer, *J. Org. Chem.*, 1974, **39**, 2979; T. Courtney, D. E. Johnston, M. A. McKervey, and J. J. Rooney, *J.C.S. Perkin I*, 1972, 2691; (c) triamantane: V. Z. Williams, jun., P. v. R. Schleyer, G. J. Gleicher, and L. B. Rodewald, *J. Amer. Chem. Soc.*, 1966, **88**, 3862.

[4] W. Burns, M. A. McKervey, and J. J. Rooney, *J.C.S. Chem. Comm.*, 1975, 965.

[5] T. M. Gund, P. v. R. Schleyer, G. D. Unruh, and G. L. Gleicher, *J. Org. Chem.*, 1974, **20**, 2995.

[6] H. Koch and W. Haaf, *Annalen*, 1958, **618**, 251.

[7] For earlier examples of the construction of a five-membered ring on the adamantane periphery using the keto-carbenoid insertion reaction, see J. K. Chakrabarti, S. S. Szinai, and A. Todd, *J. Chem. Soc.* (*C*), 1970, 1303; D. Farcasiu, E. Wiskott, E. Osawa, W. Thielecke, E. M. Engler, J. Slutsky, P. v. R. Schleyer, and G. J. Kent, *J. Amer. Chem. Soc.*, 1974, **96**, 4669; this route was also used in the synthesis of the olefin (**4**) (ref. **4**).

[8] P. J. Roberts and G. Ferguson, in preparation.