

Synthesis and X-Ray Crystal Structure of a (C_2)- C_{20} -Hexaquinane Derivative, a Potential Dodecahedrane Precursor

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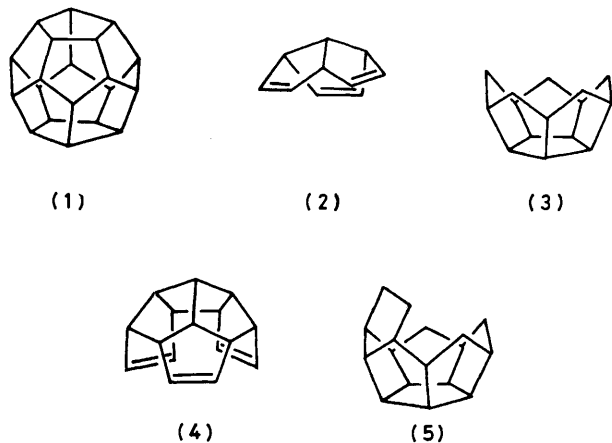
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Summary In an iterative synthesis utilising four reagents, *cis*-bicyclo[3.3.0]octane-2,6-dione has been converted into a (C_2)- C_{20} -hexaquinane derivative, a potential precursor of the $C_{20}H_{20}$ pentagonal polycycle dodecahedrane, the all-*syn-cis*-stereochemistry having been established by X-ray diffraction.

EFFORTS to synthesise the $C_{20}H_{20}$ regular (pentagonal) polycycle, dodecahedrane (**1**),¹ have produced a variety of new ways of assembling mutually *cis*-fused cyclopentane rings, resulting in potentially useful intermediates such as the C_{10} -triquinacene (**2**),² the C_{15} -peristylane (**3**),³ the C_{16} -hexaquinane (**4**),⁴ and the C_{17} -heptaquinane (**5**),⁵ and while the parent molecule is still unknown, Paquette and his co-

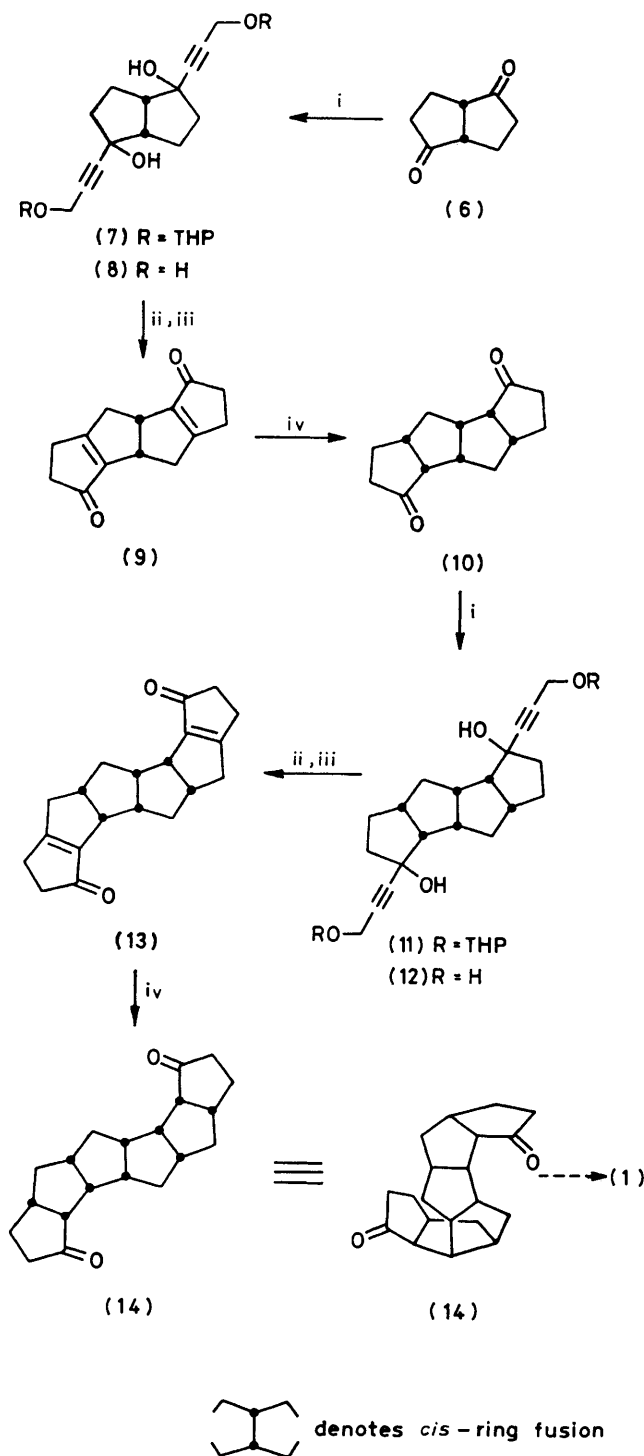
workers⁶ have produced the first compound with the dodecahedrane nucleus in an elegant synthesis of the 1,6-dimethyl derivative. The immediate objective of the work described here was the rapid construction of an intermediate containing all twenty carbon atoms in an array of six cyclopentane rings with the all-*cis-syn*-fusion essential for eventual transformation into dodecahedrane. We report the first preparation of a C₂₀-hexaquinane using an iterative approach and four reagents.



Reaction of *cis*-bicyclo[3.3.0]octane-2,6-dione (6)⁷ with the Grignard derivative of tetrahydropyran-2-yloxypropyne gave the adduct (7) (90%) from which the protecting groups could be removed quantitatively by treatment with H⁺-Amberlite resin in methanol at room temperature. Treatment of the resulting tetraol (8) with a solution of phosphorus pentoxide in methanesulphonic acid⁸ (mole ratio 1:6) for 5 h at room temperature led to double dehydrative cyclisation and the crystalline tetraquinane derivative (9), m.p. 205.0—206.5 °C, was isolated in 25% yield. Hydrogenation of (9) in ethyl acetate containing palladium produced a saturated diketone (72%), m.p. 100—101 °C, for which the all-*cis*-stereochemistry depicted in (10) was expected on the basis of steric control of the approach of hydrogen to the olefinic bonds, though this was not confirmed until later.

To continue the synthesis the tetracyclic diketone (10) was subjected to the same sequence of reactions. Thus condensation with the Grignard reagent produced the adduct (11) quantitatively; deprotection of (11) released the tetraol (12) quantitatively; dehydrative cyclisation of (12) produced the crystalline C₂₀-hexaquinane derivative (13) (45%), m.p. 240—241 °C; and hydrogenation of (13) over palladium afforded the saturated diketone (14), m.p. 215—218 °C in 64% yield. The ¹³C n.m.r. spectrum of (14) exhibited ten resonances, suggesting the presence of a C₂ symmetry axis, and the all-*syn-cis*-configuration about the ring junctions was established by a single-crystal X-ray diffraction analysis.

Crystals of (14), C₂₀H₂₆O₂, are monoclinic, $a = 21.889(3)$, $b = 6.1469(8)$, $c = 11.990(2)$ Å, $\beta = 105.06(1)^\circ$, $U = 1557.8$ Å³, $Z = 4$, $D_c = 1.27$ g cm⁻³, λ (Mo-K α) = 0.71069 Å, $\mu = 0.43$ cm⁻¹, $F(000) = 648$. Space group $C2/c$ (C_{2h}^6 , No. 15) from E statistics and systematic absences (hkl , $h + k = 2n + 1$, $h0l$, $l = 2n + 1$). The structure was solved by direct methods and refined by full-matrix least-squares



SCHEME. Reagents: i, BrMgC≡CCH₂OTHP; ii, Amberlite, MeOH; iii, P₂O₅, MeSO₃H; iv, H₂, Pd. THP = tetrahydropyran-2-yl.

calculations, using 1363 diffractometer data with $I > 3\sigma(I)$ and unit weights. The C and O atoms were allowed anisotropic thermal motion; the H atoms, located from difference syntheses, were included in geometrically idealized positions

but not refined in the calculations. The final R value is 0.067.†

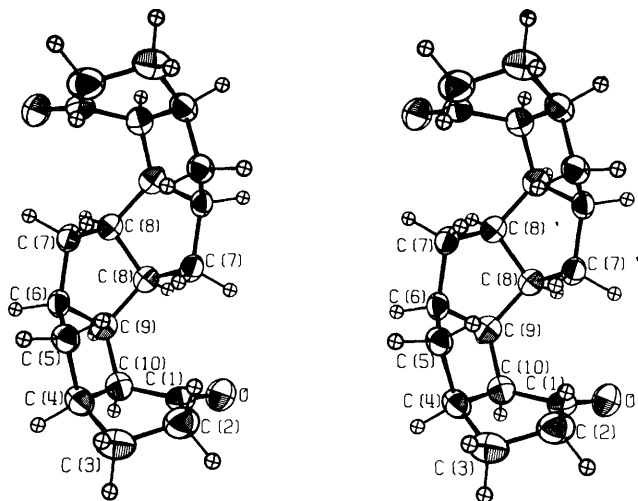


FIGURE. Stereoview of (14) showing the crystallographic numbering scheme.

The crystal structure of (14) contains discrete molecules lying on a twofold axis and separated by normal van der Waals distances. The molecule (Figure) has an 'opened out' conformation arising from the relief of severe intramolecular overcrowding of the keto-group [C(1)–O] with the C(7')H₂ moiety. There are short intramolecular contacts [O...C(7') 3.15, C(1)...C(7') 3.08 Å] similar to those observed in other severely overcrowded hydrocarbons and the exocyclic C–C–C bond angles at C(8), C(9), and C(10) are much larger than tetrahedral values [119.2, 123.4, and 120.2(2)°, respectively]. If the molecule had not adopted the conformation shown in the Figure even shorter contacts would have resulted. As a consequence of the distortion and twisting to relieve steric strain, the C(3) and C(3') atoms are separated by 8.42 Å. The molecule thus has advantages and disadvantages as an intermediate in dodecahedrane synthesis, the most relevant of the former being the proximity of the carbonyl groups to the C(7) and C(7') carbon atoms between which further C–C single bond formation is envisaged.

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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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⁸ Cyclisation conditions previously used by G. A. MacAlpine, R. A. Raphael, A. Shaw, A. W. Taylor, and H. J. Wild, *J. Chem. Soc., Perkin Trans. 1*, 1976, 410, and P. E. Eaton and R. H. Mueller, *J. Am. Chem. Soc.*, 1972, **94**, 1015.