Crystal and Molecular Structural Studies of (±)- and *meso*-Bivalvane

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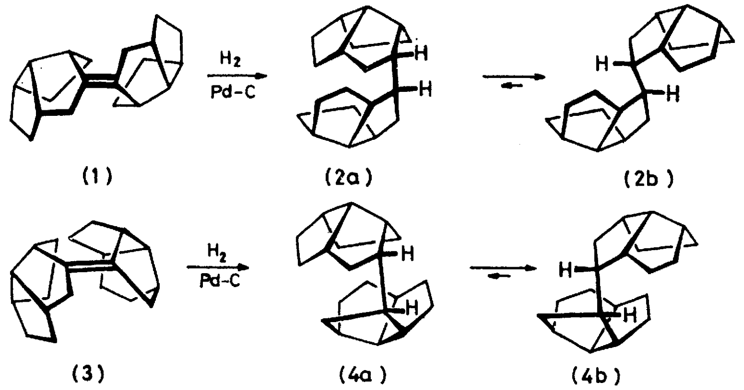
The crystal and molecular structures of (±)- and *meso*-bivalvane have been determined by single-crystal three-dimensional *X*-ray diffraction methods. The (±)-hydrocarbon (2) crystallizes in the monoclinic space group $P2_1/c$ with lattice parameters a = 9.779(1), b = 17.219(2), c = 9.635(1) Å, and β = 99.89(1)°. The structure was refined to R 0.049 for 1 853 observed reflections. The *meso*-hydrocarbon (4) is also monoclinic, space group $P2_1/n$, with Z = 2 in a cell of dimensions a = 6.377(1), b = 6.306(1), c = 19.553(2) Å, and β = 90.87(1)°. The molecule spans a crystallographic inversion centre. Refinement converged at R 0.039 for 928 observed reflections. Both bivalvanes adopt strain-free extended conformations, the triquanane-part structures of which appear to be regular in their geometry.

CATALYTIC hydrogenation of the tetrasubstituted olefins (1) and (3) over rhodium on carbon at 50 p.s.i. for several days has previously been reported to give the pentasecododecahedranes (2) and (4).[1] The colloquial names (±)- and *meso*-bivalvane have been suggested for these saturated hydrocarbons and are adopted herein.† As catalytic hydrogenation of either (1) or (3) proceeds and the pair of sp^2-hybridized carbons acquire tetrahedral character, enormous steric compression develops on the opposite side of the molecule where the two perhydrotriquinacene units are brought into close proximity. In fact, molecular models suggest that saturation of the double bond from the *exo*-face might well result in an enmeshing of the ten *endo*-protons (five from each half). If this were so, and if subsequent rotation about the single bond interconnecting the two structural halves were thereby hindered, then the bivalvanes could be locked in the conformations given by (2a) and (4a). Alternatively, these molecules could still have flexibility adequate to allow σ bond rotation and adoption of the much less sterically congested topologies illustrated by (2b) and (4b). Spectral studies in search of anomalously high infrared C–H stretching frequencies, unusual proton chemical shifts and coupling constants, and the like, proved inconclusive.[1]

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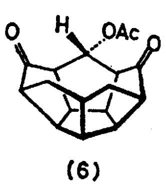

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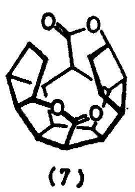

(7)

To clarify this question and gain some insight into the detailed structural features of these polyquinanes, we undertook determination of the *X*-ray crystal structures of (2) and (4). Despite a recent surge of interest in the chemistry of unusual multiply fused five-membered ring systems,[2] reliable three-dimensional information is currently available only for triquinacene (5),[3] the functionalized perstylane (6),[4,5] and dilactone (7).[6,7]

EXPERIMENTAL

Synthesis.—Both (±)-bivalvane (2) and *meso*-bivalvane (4) were prepared as previously described,[1] and recrystallized from acetone as monoclinic crystals, m.p. 85—85.5 (2) and 134—134.5 °C (4).

Crystal Data.—*±-Isomer*, (2). $C_{20}H_{30}$, M = 270.46, Monoclinic, a = 9.779(1), b = 17.219(2), c = 9.635(1) Å, β = 99.89(1)°. D_m = 1.12 g cm^{-3}, Z = 2. Space group $P2_1/c$. Cu-K_α *X*-radiation, λ = 1.54178 Å.

meso-Isomer, (4). $C_{20}H_{30}$, M = 270.46, Monoclinic, a = 6.377(1), b = 6.306(1), c = 19.553(2) Å, β = 90.87(1)°, D_m = 1.14 g cm^{-3}, Z = 2. Space group $P2_1/n$ (alternative setting of $P2_1/c$).

Accurate lattice measurements for the (±)-isomer (2)

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† The names suggested for (2) and (4) by Chemical Abstracts are (±)- and *meso-endo,endo*-eicosahydro-1,1′-bicyclopenta[*cd*]-pentalene. We thank Dr. Kurt Loenig for his assistance in this matter.

were obtained from a least-squares fitting of fifteen moderate-angle 2θ values. Of the 2 243 unique diffraction maxima measured, 1 853 (83%) were considered observed having $I \geqslant 3\sigma(I)$, and were corrected for Lorentz, polarization, and background effects.

A trial structure was found through use of a multi-solution sign-determining procedure.[8] All carbon atoms were clearly identifiable in the first E synthesis. Hydrogen atoms were located from a difference-Fourier synthesis. Full-matrix least-squares refinement with anisotropic temperature factors for carbon and isotropic for hydrogen atoms converged to an unweighted crystallographic residual of 0.049 for the observed reflections.

In the case of the *meso*-isomer (4), a least squares fit of fifteen moderate-angle 2θ values gave precise cell constants. The only way to reconcile the space group ($P2_1/n$) and density (*ca.* 1.14) was to assume that half the molecule formed the asymmetric unit, the other half being generated by the point-group symmetry. Thus the molecule had to span a crystallographic inversion centre and was the *meso*-isomer. Data were collected and the structure solved and refined as before with 928 (79%) of the total of 1 170 diffraction maxima used in the analysis which converged at R 0.039.

TABLE 1

Final atom fractional co-ordinates for (±)- and *meso*-bivalvane, with estimated standard deviations in parentheses

(*a*) (±)-Bivalvane

Atom	*x*	*y*	*z*
C(1)	0.660 8(2)	0.119 2(1)	−0.050 9(2)
C(2)	0.676 0(2)	0.032 6(1)	−0.0912 (2)
C(3)	0.720 9(2)	0.035 6(1)	−0.236 9(2)
C(4)	0.811 7(2)	0.108 6(1)	−0.226 4(2)
C(5)	0 738 9(2)	0.167 8(1)	−0.146 3(2)
C(6)	0.836 6(3)	0.220 6(1)	−0.046 5(2)
C(7)	0.872 6(3)	0.173 0(2)	0.086 1(3)
C(8)	0.739 9(2)	0.129 3(1)	0.101 6(2)
C(9)	0.763 5(3)	0.046 8(2)	0.158 6(2)
C(10)	0.782 7(2)	−0.000 9(1)	0.029 7(2)
C(1′)	0.775 0(2)	−0.167 1(1)	−0.386 3(2)
C(2′)	0.701 8(2)	−0.112 2(1)	−0.295 7(2)
C(3′)	0.788 8(2)	−0.037 4(1)	−0.282 9(2)
C(4′)	0.834 2(2)	−0.032 4(1)	−0.426 7(2)
C(5′)	0.870 7(2)	−0.116 6(1)	−0.460 8(2)
C(6′)	0.837 7(3)	−0.138 9(2)	−0.616 2(2)
C(7′)	0.684 4(3)	−0.158 5(2)	−0.638 8(2)
C(8′)	0.662 1(2)	−0.200 5(1)	−0.504 1(3)
C(9′)	0.524 5(2)	−0.181 1(2)	−0.456 0(3)
C(10′)	0.553 2(2)	−0.104 6(1)	−0.378 4(3)
H(1)	0.566(3)	−0.137(1)	−0.062(2)
H(2)	0.591(2)	0.002(1)	−0.095(2)
H(3)	0.635(2)	0.046(1)	−0.307(2)
H(4A)	0.824(2)	0.128(1)	−0.218(3)
H(4B)	0.917(2)	0.098(1)	−0.161(2)
H(5)	0.673(2)	0.198(1)	−0.211(2)
H(6A)	0.780(3)	0.267(2)	−0.028(3)
H(6B)	0.922(3)	0.236(2)	−0.087(3)
H(7A)	0.908(3)	0.205(2)	0.168(3)
H(7B)	0.948(3)	0.135(2)	0.073(2)
H(8)	0.681(3)	0.158(1)	0.152(3)
H(9A)	0.679(3)	0.025(2)	0.189(3)
H(9B)	0.848(3)	0.042(1)	0.237(3)
H(10A)	0.678(3)	−0.060(2)	0.044(3)
H(10B)	0.880(3)	0.007(2)	0.013(3)
H(1′)	0.827(2)	−0.205(1)	−0.332(2)
H(2′)	0.698(2)	−0.134(1)	−0.201(3)
H(3′)	0.875(2)	−0.048(1)	−0.212(2)
H(4′A)	0.747(2)	−0.011(1)	−0.507(2)
H(4′B)	0.914(2)	0.003(1)	−0.428(2)
H(5′)	0.970(3)	−0.123(1)	−0.422(2)
H(6′A)	0.862(3)	−0.098(2)	−0.682(3)
H(6′B)	0.888(2)	−0.186(2)	−0.632(2)
H(7′A)	0.628(3)	−0.111(2)	−0.651(2)
H(7′B)	0.653(3)	−0.188(2)	−0.729(3)
H(6′)	0.677(3)	−0.254(2)	−0.519(3)
H(9′A)	0.444(3)	−0.178(2)	−0.541(3)
H(9′B)	0.509(3)	−0.223(2)	−0.387(3)
H(10′A)	0.550(2)	−0.058(2)	−0.449(3)
H(10′B)	0.489(3)	−0.092(2)	−0.312(3)

TABLE 1 (*Continued*)

(*b*) *meso*-Bivalvane

Atom	*x*	*y*	*z*
C(1)	0.202 5(3)	0.400 5(3)	0.358 5(1)
C(2)	0.225 4(3)	0.402 1(3)	0.437 7(1)
C(3)	0.028 1(3)	0.517 6(3)	0.462 6(1)
C(4)	−0.139 8(3)	0.449 8(3)	0.410 2(1)
C(5)	−0.029 5(3)	0.451 0(3)	0.341 1(1)
C(6)	−0.099 7(4)	0.277 0(4)	0.291 6(1)
C(7)	0.025 8(4)	0.083 5(4)	0.214 9(1)
C(8)	0.242 1(3)	0.169 8(3)	0.224 5(1)
C(9)	0.347 6(4)	0.061 1(4)	0.295 7(1)
C(10)	0.246 3(3)	0.166 7(4)	0.457 3(1)
H(1)	0.295(3)	0.502(3)	0.338(1)
H(2)	0.353(4)	0.470(3)	0.452(1)
H(3)	0.055(3)	0.674(4)	0.456(1)
H(4A)	−0.266(4)	0.540(4)	0.410(1)
H(4B)	−0.187(3)	0.304(4)	0.421(1)
H(5)	−0.045(3)	0.594(4)	0.321(1)
H(6A)	−0.250(6)	0.252(4)	0.291(1)
H(6B)	−0.062(4)	0.309(4)	0.246(2)
H(7A)	−0.042(3)	0.022(3)	0.354(1)
H(7B)	0.035(4)	−0.034(4)	0.279(1)
H(8)	0.331(3)	0.165(3)	0.295(1)
H(9A)	0.504(4)	0.090(4)	0.398(1)
H(9B)	0.327(4)	−0.093(5)	0.396(1)
H(10A)	0.327(4)	0.145(4)	0.501(1)
H(10B)	0.102(4)	0.099(4)	0.462(1)

TABLE 2

Interatomic distances (Å) in (±)-(2) and *meso*-bivalvane (4) with estimated standard deviations in parentheses. Values for (4) follow those for (2)

C(1)–C(2)	1.555(3)	1.555(2)
C(1)–C(5)	1.539(3)	1.546(3)
C(1)–C(8)	1.548(3)	1.551(3)
C(2)–C(3)	1.542(3)	1.539(3)
C(2)–C(10)	1.537(3)	1.539(3)
C(3)–C(4)	1.532(3)	1.532(3)
C(3)–C(3′)	1.523(3)	1.529(3)
C(4)–C(5)	1.528(3)	1.534(3)
C(5)–C(6)	1.532(3)	1.527(3)
C(6)–C(7)	1.508(3)	1.525(3)
C(7)–C(8)	1.530(4)	1.526(3)
C(8)–C(9)	1.526(3)	1.526(3)
C(9)–C(10)	1.527(3)	1.529(3)
C(1′)–C(2′)	1.543(3)	
C(1′)–C(5′)	1.542(3)	
C(1′)–C(8′)	1.551(3)	
C(2′)–C(3′)	1.537(3)	
C(2′)–C(10′)	1.538(3)	
C(3′)–C(4′)	1.528(3)	
C(4′)–C(5′)	1.542(3)	
C(5′)–C(8′)	1.525(3)	
C(6′)–C(7′)	1.516(4)	
C(7′)–C(8′)	1.534(4)	
C(8′)–C(8)	1.533(4)	
C(9′)–C(10′)	1.517(4)	

RESULTS AND DISCUSSION

The atom co-ordinates for (2) and (4) are listed in Table 1, and significant intramolecular bond lengths and bond angles are in Tables 2 and 3. Figures 1 and 2 illustrate the two molecules and show the atom numbering system used in the crystallographic analysis.*

TABLE 3

Bond angles (°) in (±)- (2) and *meso*-bivalvane (4), with estimated standard deviations in parentheses. Values for (2) precede those for (4)

C(2)–C(1)–C(5)	107.1(2)	109.1(1)
C(2)–C(1)–C(8)	106.9(2)	107.2(1)
C(5)–C(1)–C(8)	106.7(2)	106.6(1)
C(1)–C(2)–C(3)	104.5(2)	104.7(1)
C(1)–C(2)–C(10)	104.6(2)	104.4(1)
C(3)–C(2)–C(10)	116.2(2)	116.4(1)
C(2)–C(3)–C(4)	102.7(2)	102.8(1)
C(2)–C(3)–C(3′)	116.3(2)	116.0(2)
C(4)–C(3)–C(2′)	114.8(2)	115.4(2)
C(3)–C(4)–C(5)	105.4(2)	105.3(1)
C(1)–C(5)–C(4)	105.1(2)	104.8(1)
C(1)–C(5)–C(6)	105.5(2)	105.2(2)
C(4)–C(5)–C(6)	114.7(2)	115.0(2)
C(5)–C(6)–C(7)	103.8(2)	103.7(2)
C(6)–C(7)–C(6)	105.8(2)	104.9(2)
C(1)–C(6)–C(7)	104.8(2)	105.1(2)
C(1)–C(8)–C(9)	104.9(2)	104.7(1)
C(7)–C(8)–C(9)	114.5(2)	115.0(2)
C(8)–C(9)–C(10)	103.9(2)	103.7(2)
C(2)–C(10)–C(9)	104.6(2)	105.0(2)
C(2′)–C(1′)–C(5′)	107.2(2)	
C(2′)–C(1′)–C(8′)	107.4(2)	
C(5′)–C(1)–C(8′)	106.3(2)	
C(1′)–C(2′)–C(3′)	104.7(2)	
C(1′)-C(2′)–C(10′)	104.4(2)	
C(9′)–C(2′)–C(10′)	115.5(2)	
C(3)–C(3′)–C(2′)	116.9(2)	
C(3)–C(3′)–C(4′)	115.2(2)	
C(2′)–C(3′)–C(4′)	102.6(1)	
C(3′)–C(4′)–C(5′)	104.7(2)	
C(1′)–C(5′)–C(4′)	104.5(2)	
C(1′)–C(5′)–C(6′)	105.8(2)	
C(4′)–C(5′)–C(6′)	115.4(2)	
C(5′)–C(6′)–C(7′)	103.5(2)	
C(6′)–C(7′)–C(8′)	105.3(2)	
C(1′)–C(8′)–C(7′)	104.9(2)	
C(1′)–C(8′)–C(9′)	104.4(2)	
C(7′)–C(8′)–C(9′)	114.3(2)	
C(8′)–C(9′)–C(10′)	103.9(2)	
C(2′)–C(10′)–C(9′)	105.0(2)	

(±)-*Bivalvane* (2). This clearly adopts conformation (2b) in the crystalline state. In general, the bond distances within the two perhydrotriquinane halves of the structure agree well with generally accepted values. The mean lengths of the twelve carbon–carbon bonds in the lower (left) and upper (right) $C_{10}H_{15}$ moieties are identical within experimental error (1.534 Å). The interconnective C(3)–C(3′) bond is somewhat shorter (1.523 Å), but still as expected. Certainly, no molecular crowding is in evidence. The mean interior bond angle within the six cyclopentane rings of the molecule is 105.0° which approximates rather closely the calculated value (108.0°) for an idealized regular pentagon. The external angles between the folds of the five-membered rings (*e.g.*, C(3)–C(2)–C(10)) are conspicuously uniform, mean 115.4°. Given the close structural similarity between the upper and lower halves of the molecule and their stereochemical relationship (necessarily of the same chirality), the virtual equivalence of the two triquinane ring geometries is fully expected.

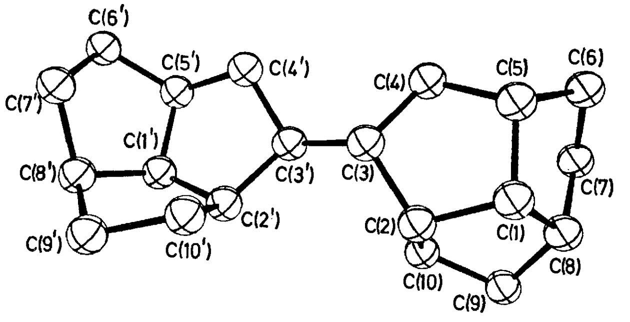

FIGURE 1 A computer generated perspective drawing of (±)-bivalvane (2); hydrogen atoms are omitted for clarity.

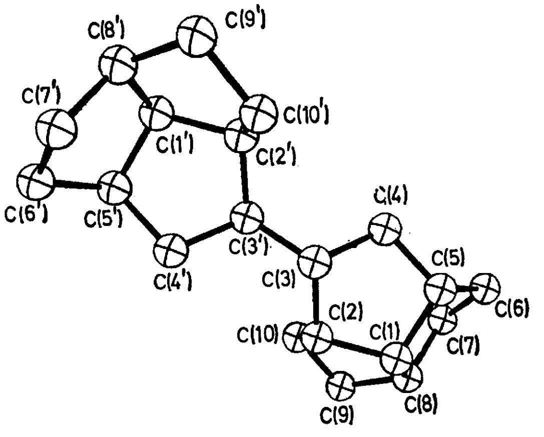

FIGURE 2 A computer generated perspective drawing of *meso*-bivalvane (4). The molecule utilizes a crystallographic centre of symmetry and hydrogens are omitted for clarity

No abnormally short intermolecular contacts or unusually high electron densities were noted in the final difference-Fourier synthesis.

meso-*Bivalvane* (4). Because the molecule adopts a crystallographic inversion centre, the primed atoms share an identity with their unprimed counterparts. Although hydrogen atoms are excluded from Figure 2, their positions were rather well resolved (see thermal parameters listed in Supplementary Publication).

As does (2), *meso*-bivalvane (4) adopts an extended conformation (4b). No molecular overcrowding is apparent, as reflected in part on the central σ [C(3)–C(3′)] bond distance (1.529 Å). The mean value of twelve carbon–carbon bonds is 1.536 Å in length, and of the interior bond angles 105.4°. Both triquinacene halves may therefore be considered to be structurally unperturbed in view of the good agreement with generally accepted values. Again, no abnormally short intermolecular contacts or high electron densities were apparent.

The three-dimensional *X*-ray analyses of (±)- and *meso*-bivalvane reveal that the conformational patterns adopted by these molecules are unmistakably those in which the amount of residual strain is minimal. As such, we now have a basis for assessing the structural features of sterically unperturbed triquinanes. An apparent consequence of the presence of structurally

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* Final observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22383 (16 pp., 1 microfiche). For details see Notice to Authors No. 7, in *J.C.S. Perkin II*, 1978, Index issue.

enforced steric strain is molecular deformation away from ideal geometry. Both (6) and (7) which project ' rim ' substituents toward the interior of their cavities, yet have low conformational flexibility, have been shown to be distorted from symmetric bowl shapes.[5,7] The extent to which crystal packing forces contribute to the observed deformations remains unknown, as usual. Nonetheless, these hexaquinane derivatives serve as useful reference points for an eventual assessment of the pentagonal dodecahedrane structure. The perfect icosahedral (I_h) symmetry of the still unknown $C_{20}H_{20}$ sphere, in tandem with a lack of comparable interior steric congestion, might be expected not to force its twelve constituent pentagons to deviate from planarity.[9]

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