

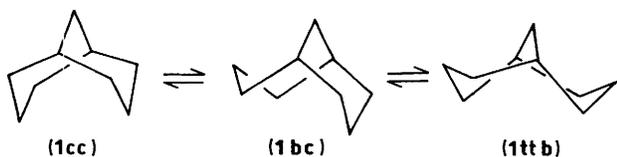
## Preparation and Crystal Structure of a Twin Twist-Boat Bicyclo[3.3.1]nonane Monohydrate

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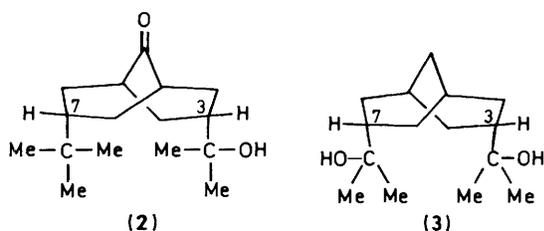
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Reduction of 3,3,7,7-tetramethyl-2,6-dimethylenebicyclo[3.3.1]nonane bis(epoxide) (7) with lithium aluminium hydride affords a mixture of *exo*-2,*exo*-6-dihydroxy-2,3,3,6,7,7-hexamethylbicyclo[3.3.1]nonane (8) and *exo*-2-hydroxy,*exo*-6-hydroxymethyl-2,3,3,7,7-pentamethylbicyclo[3.3.1]nonane (9). The diol (8) was obtained as its monohydrate, the crystal structure of which [ $P\bar{1}$ ;  $a = 7.388(2)$ ,  $b = 9.292(2)$ ,  $c = 11.466(2)$  Å;  $\alpha = 80.52(2)$ ,  $\beta = 89.68(1)$ ,  $\gamma = 70.85(2)^\circ$ ;  $Z = 2$ ] was determined with a final  $R = 0.049$ . In the solid state the bicyclo[3.3.1]nonane skeleton of (8) exists in a flattened twin twist-boat conformation and four neighbouring diols are linked by a fully hydrogen-bonded water molecule. The co-crystallisation behaviour shown by (8) is quite different from the helical tubuland arrangement exhibited by other alicyclic diols closely related in structure, but is fully in accord with that of a previously recognised family of alcohol hemihydrates based on the pentamethylethanol structure.

It is well established<sup>1</sup> that the lowest energy conformation of bicyclo[3.3.1]nonane is the twin chair arrangement (1cc) and that simple derivatives<sup>2</sup> of this ring system, unsubstituted at C-3 and C-7, also generally adopt this conformation. Force field calculations on bicyclo[3.3.1]nonane indicate that its boat-chair conformation (1bc) is 9.7 kJ mol<sup>-1</sup> above the twin chair and that the next energy minimum, the twin twist-boat (1ttb), is a further 21.0 kJ mol<sup>-1</sup> higher in energy.<sup>3</sup>



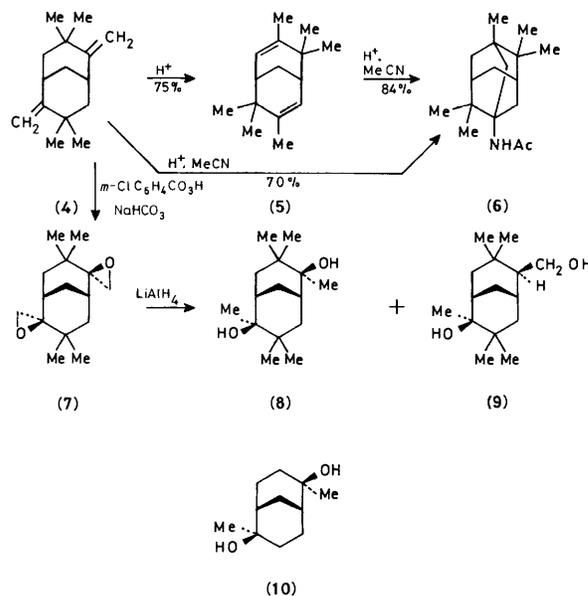
Although the latter high energy conformer has been the subject of theoretical investigation, and has been invoked in explaining several reactions of bicyclo[3.3.1]nonane derivatives,<sup>4</sup> detailed experimental measurements have been relatively limited.



Peters *et al.* have reported detailed variable temperature n.m.r. studies of several conformational equilibria,<sup>5</sup> and in particular have used n.m.r. to investigate the two compounds (2) and (3) (bearing especially bulky *endo*-3- and *endo*-7-substituents) which exist in the twin boat form as their lowest energy conformer.<sup>6</sup> The crystal structure of one of these, *endo*-3,*endo*-7-bis(2-hydroxypropan-2-yl)bicyclo[3.3.1]nonane (3), has been determined.<sup>7</sup> This provided excellent confirmation of earlier predictions based on n.m.r. and molecular mechanics studies, in particular that the energy minimum is the twist arrangement and that the rings are significantly flattened in this conformation.

For some time we have been interested in conformations of the

bicyclo[3.3.1]nonane skeleton other than the twin chair and, in particular, the potential involvement of such arrangements in intramolecular cyclisation and rearrangement processes.<sup>8</sup> Recently we have examined 3,3,7,7-tetramethyl derivatives of the system where the twin chair is ruled out through steric crowding of the *endo*-3- and *endo*-7-methyl groups, and have reported<sup>9</sup> that 3,3,7,7-tetramethyl-2,6-dimethylenebicyclo[3.3.1]nonane (4) undergoes an efficient one-flask rearrangement and Ritter reaction with acetonitrile to yield 1-acetamido-2,2,5,6,6-pentamethyladamantane (6) *via* the diene intermediate (5).



As part of this investigation we became interested in *exo*-2,*exo*-6-dihydroxy-2,3,3,6,7,7-hexamethylbicyclo[3.3.1]nonane (8) and its likely properties. A number of alicyclic diols closely related in structure to (8), including the nor-methyl diol (10), form a helical tubuland structure in the crystalline state.<sup>10,11</sup> Would the diol (8) show similar structural and inclusion behaviour? Furthermore, although the *endo* substituents of (8) are only modest in size we considered that it would exist in the elusive twin boat conformation due to steric crowding between

**Table 1.** Fractional co-ordinates for the non-hydrogen atoms of *exo*-2,*exo*-6-dihydroxy-2,3,3,6,7,7-hexamethylbicyclo[3.3.1]nonane monohydrate

Atomic parameters and standard deviations

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
O(1)	0.105 1(2)	0.872 8(2)	0.362 7(1)
O(2)	0.369 7(2)	0.196 4(2)	0.379 4(1)
O(3)	0.747 7(2)	0.013 3(2)	0.459 2(1)
C(1)	0.072 7(3)	0.637 6(2)	0.316 4(2)
C(2)	0.120 6(3)	0.786 1(2)	0.267 5(2)
C(3)	0.337 2(3)	0.744 2(2)	0.228 9(2)
C(4)	0.419 9(3)	0.571 4(2)	0.215 9(2)
C(5)	0.394 0(3)	0.451 2(2)	0.319 7(2)
C(6)	0.337 9(3)	0.319 5(2)	0.278 6(2)
C(7)	0.115 2(3)	0.375 9(2)	0.241 0(2)
C(8)	0.031 8(3)	0.554 9(2)	0.217 7(2)
C(9)	0.241 0(3)	0.529 6(2)	0.399 4(2)
C(10)	-0.030 1(4)	0.888 6(3)	0.171 0(2)
C(11)	0.355 5(4)	0.838 6(3)	0.109 8(2)
C(12)	0.467 9(3)	0.775 5(3)	0.318 4(2)
C(13)	0.471 9(4)	0.252 7(3)	0.185 2(2)
C(14)	0.077 5(4)	0.322 8(3)	0.127 0(2)
C(15)	-0.001 4(3)	0.312 4(3)	0.335 0(2)

the various *endo* methyl groups in potential twin chair or boat-chain arrangements.

The synthetic approach chosen was epoxidation of the diene **9** (**4**) followed by reductive ring opening using lithium aluminium hydride. Initial attempts to epoxidise (**4**) using *m*-chloroperbenzoic acid in chloroform were not successful. The i.r. spectra of the products indicated loss of the olefinic signals but little in the way of bands ascribable to epoxide groups. Instead, intense carbonyl and hydroxy groups were present, suggesting that bis(epoxide) (**7**) had been produced but that it had undergone subsequent reaction.

Successful epoxidation was effected by switching to a two-phase system, whereby the diene (**4**) was treated with a solution of the peracid in dichloromethane stirred vigorously with a solution of aqueous sodium hydrogen carbonate.

Reduction of the crude bis(epoxide) (**7**) in ether using lithium aluminium hydride proposed a mixture containing two major polar products whose t.l.c. behaviour was almost identical. Using ethyl acetate as eluant, the lower  $R_F$  compound (0.93) proved to be the required diol (**8**) while the higher  $R_F$  compound (0.95) also turned out to be a diol, 2-hydroxy-6-hydroxymethyl-2,3,3,7,7-pentamethylbicyclo[3.3.1]nonane (**9**) (see Experimental section for data). Ring-opening of epoxides with lithium aluminium hydride normally involves preferential attack at the lesser crowded carbon atom, resulting here in formation of the expected diol (**8**) whose stereochemistry was subsequently confirmed by *X*-ray crystallography. However in this case reduction of the more substituted carbon is competitive with this process, resulting in production of (**9**). Since it was not demonstrated that all the bis(epoxide) present had the *exo,exo* stereochemistry of (**7**), the stereochemistry of (**9**) can only be presumed to be as shown. However, since only two diols were obtained this proposal is the most reasonable one.

The two products were best separated by exploiting their differing solubility properties (see Experimental section). The

diol (**8**) was isolated as its monohydrate. The retention of the water molecule throughout recrystallisation from organic solvents, and the very sharp m.p. (149.5–150.0 °C), indicated that it was intimately involved in the crystalline hydrogen bonding arrangement. Determination of the crystal structure of the monohydrate was carried out on a sample recrystallised from acetonitrile–light petroleum.

The crystallographic numbering system used is based on the systematic numbering of the ring system and is shown in Figure 1. Fractional co-ordinates for the non-hydrogen atoms are given in Table 1, while bond lengths and angles are listed in Table 2. A complete table of position and thermal parameters has been deposited.\*

This structure determination shows (Figure 1) that the diol (**8**) monohydrate exists in a flattened twin twist-boat conformation with the various ring substituents almost eclipsed, and with C(4)/C(8) twisted inwards such that the transannular separation of the *endo*-4 and *endo*-8 hydrogen atoms is only 2.07 Å. The extent of twisting and ring flattening in (**8**) may be gauged from the torsion angles of its bicyclic skeleton (Table 3). These effects are exacerbated over the previous twin twist-boat structure<sup>7</sup> by the presence of the *exo*-3 and *exo*-7 methyl groups, and their steric interaction with the 9-methylene group. They may also be influenced by constraints placed on the ring system by hydrogen bonding requirements.

This crystal structure clearly demonstrates that the twin twist-boat conformation of the bicyclo[3.3.1]nonane skeleton may be readily accessible for appropriate molecules lacking very bulky *endo* groups at C-3 and C-7, and therefore the involvement of this conformation in bicyclo[3.3.1]nonane chemistry may be more frequent than previously realised.<sup>4</sup> On the other hand, it is even clearer that the crystal structure of (**8**) monohydrate bears no similarity at all to the helical tubuland inclusion system displayed by diol (**10**) and structurally related analogues.<sup>10,11</sup>

Some years ago, Hatt<sup>12</sup> recognised the existence of a family of stable hemihydrates formed by monohydric alcohols close in structure to pentamethylethanol in which the water molecule acted as a hydrogen bonded linkage between four adjacent alcohol molecules. The molecular packing in the monohydrate (Figure 2) reveals an analogous situation. Both enantiomers of (**8**) are arranged with their C-9 bridge up or down such that all ring substituents are orientated in the same direction, and the fully hydrogen bonded water molecules act as bridging links between four neighbouring diols.

Since the diol (**8**) may be regarded as having a structure very close to a doubly linked dimeric analogue of pentamethylethanol (Figure 3), its isolation as the monohydrate is in full accord with the steric and hydrogen bonding requirements of the compounds discussed by Hatt. These factors clearly dominate over those which might otherwise have resulted in the diol adopting a helical tubuland crystal structure as occurs for other diols of closely related structure such as (**10**). Although the diol (**8**) contains nearly all of the molecular features identified as structural prerequisites<sup>13</sup> for the helical tubuland system, these results demonstrate that additional substituent groups on the periphery of the cyclic system are not favourable. However, the alternative co-crystallisation behaviour shown by (**8**) supports our view that distinct families of such materials exist and that it is possible to relate their behaviour and properties to definite molecular determinants.

## Experimental

M.p.s. were determined on a Kofler hot-stage microscope and are uncorrected. <sup>1</sup>H (100 MHz) and <sup>13</sup>C (25.1 MHz) N.m.r. spectra were recorded on a JEOL JNM-FX100 spectrometer, and are reported as chemical shifts ( $\delta$ ) relative to internal SiMe<sub>4</sub>. The substitution of carbon atoms was determined by off-resonance

\* 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 article.

**Table 2.** Bond lengths and angles for the diol (**8**) monohydrate

## Interatomic distances and standard deviations (Å)

C(2)–O(1)	1.443(2)	C(10)–C(2)	1.531(3)
C(2)–C(1)	1.551(3)	C(11)–C(3)	1.529(3)
C(3)–C(2)	1.596(3)	C(12)–C(3)	1.537(3)
C(4)–C(3)	1.551(3)	C(13)–C(6)	1.522(3)
C(5)–C(4)	1.549(3)	C(14)–C(7)	1.528(3)
C(6)–O(2)	1.445(2)	C(15)–C(7)	1.539(3)
C(6)–C(5)	1.555(3)	O(1)–HO(1)	0.747(1)
C(7)–C(6)	1.592(3)	O(2)–HO(2)	0.675(1)
C(8)–C(1)	1.551(3)	O(3)–H1O(3)	0.720(1)
C(8)–C(7)	1.549(3)	O(3)–H2O(3)	0.799(1)
C(9)–C(1)	1.529(3)		
C(9)–C(5)	1.520(3)		

## Interatomic angles and standard deviations (°)

C(2)–C(1)–C(8)	113.2(2)	C(6)–C(5)–C(9)	108.2(2)
C(2)–C(1)–C(9)	107.8(2)	O(2)–C(6)–C(5)	107.4(2)
C(8)–C(1)–C(9)	110.7(1)	O(2)–C(6)–C(7)	106.6(2)
O(1)–C(2)–C(1)	107.6(2)	O(2)–C(6)–C(13)	106.5(2)
O(1)–C(2)–C(3)	106.7(2)	C(5)–C(6)–C(7)	110.9(1)
O(1)–C(2)–C(10)	106.4(2)	C(5)–C(6)–C(13)	109.9(2)
C(1)–C(2)–C(3)	111.0(2)	C(7)–C(6)–C(13)	115.1(2)
C(1)–C(2)–C(10)	109.9(2)	C(6)–C(7)–C(8)	110.4(2)
C(3)–C(2)–C(10)	114.8(2)	C(6)–C(7)–C(14)	112.1(2)
C(2)–C(3)–C(4)	110.6(2)	C(6)–C(7)–C(15)	112.6(2)
C(2)–C(3)–C(11)	112.5(2)	C(8)–C(7)–C(14)	106.8(2)
C(2)–C(3)–C(12)	112.2(2)	C(8)–C(7)–C(15)	108.8(2)
C(4)–C(3)–C(11)	106.7(2)	C(14)–C(7)–C(15)	105.8(2)
C(4)–C(3)–C(12)	108.5(2)	C(1)–C(8)–C(7)	116.5(2)
C(11)–C(3)–C(12)	106.0(2)	C(1)–C(9)–C(5)	105.8(1)
C(3)–C(4)–C(5)	117.0(2)	C(2)–O(1)–HO(1)	106.6(2)
C(4)–C(5)–C(6)	113.5(2)	C(6)–O(2)–HO(2)	111.0(2)
C(4)–C(5)–C(9)	110.5(2)	H1O(3)–O(3)–H2O(3)	97.8(2)

## Interatomic distances and standard deviations (Å) associated with hydrogen bonding

O(1) ... O(3) <sup>iii</sup>	2.822(2)	O(1) ... H1O(3) <sup>iii</sup>	2.115(2)	O(1) ... O(3) <sup>i</sup>	2.843(2)	O(3) ... HO(1) <sup>ii</sup>	2.133(2)
O(2) ... O(3)	2.816(2)	O(3) ... HO(2)	2.159(2)	O(2) ... O(3) <sup>iv</sup>	2.806(2)	O(2) ... H2O(3) <sup>iv</sup>	2.031(2)

## Interatomic angles and standard deviations (°) associated with hydrogen bonding

C(2)–O(1) ... O(3) <sup>iii</sup>	154.3(1)	C(2)–O(1) ... O(3) <sup>i</sup>	122.1(1)	O(3) <sup>i</sup> ... O(1) ... O(3) <sup>iii</sup>	83.4(1)
C(6)–O(2) ... O(3) <sup>iv</sup>	153.0(1)	C(6)–O(2) ... O(3)	119.5(1)	O(3) ... O(2) ... O(3) <sup>iii</sup>	86.4(1)
O(2) ... O(3) ... O(2) <sup>iv</sup>	93.6(1)	O(2) ... O(3) ... O(1) <sup>ii</sup>	138.8(1)	O(2) ... O(3) ... O(1) <sup>iii</sup>	112.9(1)
O(2) <sup>iv</sup> ... O(3) ... O(1) <sup>ii</sup>	113.0(1)	O(2) <sup>iv</sup> ... O(3) ... O(1) <sup>iii</sup>	94.0(1)	O(1) <sup>ii</sup> ... O(3) ... O(1) <sup>iii</sup>	96.6(1)
O(1)–HO(1) ... O(3) <sup>i</sup>	159.1(1)	O(2)–HO(2) ... O(3)	164.8(1)	O(3)–H1O(3) ... O(1) <sup>iii</sup>	167.3(1)
O(3)–H2O(3) ... O(2) <sup>iv</sup>	163.7(1)				

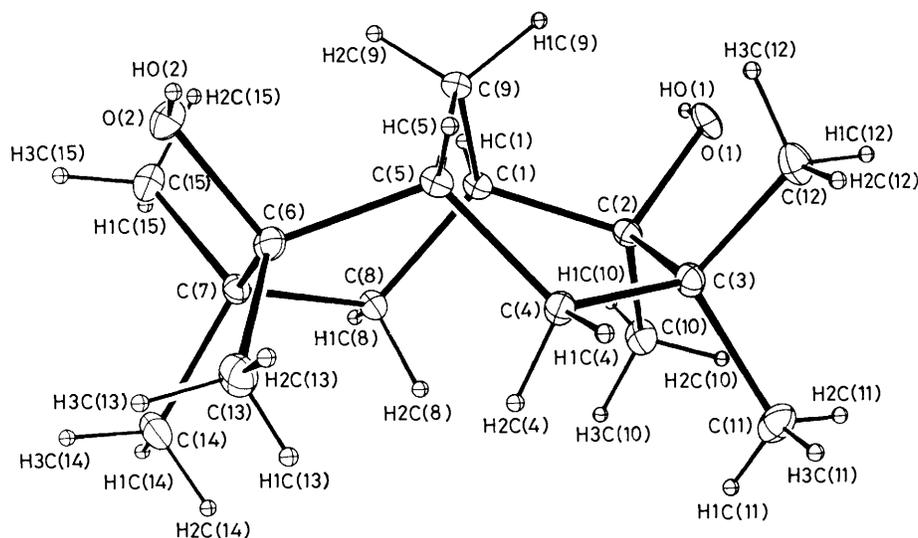
<sup>i</sup> –1 + x, 1 + y, z. <sup>ii</sup> 1 + x, –1 + y, z. <sup>iii</sup> 1 – x, 1 – y, 1 – z. <sup>iv</sup> 1 – x, –y, 1 – z.

**Table 3.** Torsion angles of the bicyclo[3.3.1]nonane skeleton of the diol (**8**) monohydrate

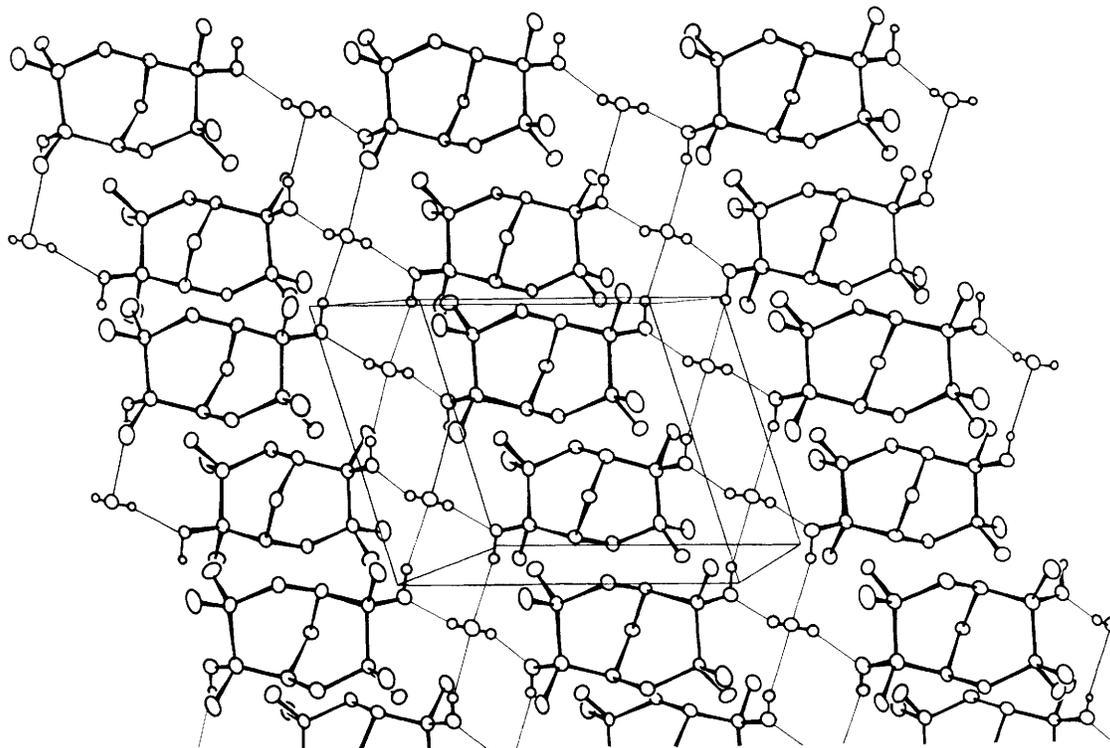
C(8)–C(1)–C(2)–C(3)	–78.6
C(9)–C(1)–C(2)–C(3)	44.1
C(2)–C(1)–C(8)–C(7)	139.6
C(9)–C(1)–C(8)–C(7)	18.4
C(2)–C(1)–C(9)–C(5)	–79.7
C(8)–C(1)–C(9)–C(5)	44.5
C(1)–C(2)–C(3)–C(4)	16.6
C(2)–C(3)–C(4)–C(5)	–49.5
C(3)–C(4)–C(5)–C(6)	138.3
C(3)–C(4)–C(5)–C(9)	16.5
C(4)–C(5)–C(6)–C(7)	–79.2
C(9)–C(5)–C(6)–C(7)	43.8
C(4)–C(5)–C(9)–C(1)	45.9
C(6)–C(5)–C(9)–C(1)	–78.9
C(5)–C(6)–C(7)–C(8)	17.9
C(6)–C(7)–C(8)–C(1)	–51.2

decoupling. Routine mass spectra were obtained on an AEI MS12 instrument, and exact masses on an MS9 instrument.

*3,3,7,7-Tetramethyl-2,6-dimethylenebicyclo[3.3.1]nonane Bis(epoxide) (7).*—A solution of sodium hydrogen carbonate (2.1 g, 25.0 mmol) in water (50 ml) was added to a solution of *m*-chloroperbenzoic acid (85% purity; 4.32 g, 21.3 mmol) in dichloromethane (50 ml). This two-phase system was cooled with an external ice-bath, stirred vigorously, and a solution of 3,3,7,7-tetramethyl-2,6-dimethylenebicyclo[3.3.1]nonane<sup>9</sup> (**4**) (2.04 g, 10.0 mmol) in dichloromethane (10 ml) added in portions over 3 min. The mixture was stirred for 6 h after which aqueous sodium sulphide (5 ml) was added to give almost immediately a negative starch-iodide test. The reaction mixture was transferred to a separating funnel and the organic layer separated. After further extraction with dichloromethane (3 × 50 ml), the combined organic extracts were washed (satd. NaHCO<sub>3</sub>, then water), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated to give the crude product as an oil. Elution through a column of neutral



**Figure 1.** The flattened twin twist-boat conformation of *exo-2,exo-6*-dihydroxy-2,3,3,6,7,7-hexamethylbicyclo[3.3.1]nonane (**8**) as present in the crystalline monohydrate. The crystallographic numbering system marked on the diagram is based on the systematic numbering of the bicyclic skeleton. Not shown in this figure is the water molecule, whose atoms are labelled O(3), H1O(3), and H2O(3)



**Figure 2.** The molecular and hydrogen bonding arrangement of the diol (**8**) and water molecules in the crystalline monohydrate. Hydrocarbon hydrogens are omitted for clarity

alumina using light petroleum-ether (2:1), followed by evaporation of solvent, gave the crude *bis(epoxide)* (**7**) (1.60 g, 68%) as a viscous oil;  $\nu_{\max}$ (film) 925s, 810s, and 735w  $\text{cm}^{-1}$ ;  $\delta_{\text{C}}$ ( $\text{CDCl}_3$ ) (major peaks only), 65.1(s), 51.6(t), 41.2(t), 36.5(d), 31.9(s), 29.3(q), 28.7(q), and 26.6(t).

**Reduction of the Bis(epoxide) (7).**—A suspension of lithium aluminium hydride (0.92 g, 24 mmol) in anhydrous ether (30 ml) was stirred at 0 °C in a flask fitted with a reflux condenser and drying tube. To this was added slowly a solution of the crude *bis(epoxide)* (**7**) (1.40 g, 5.93 mmol) in anhydrous ether (20 ml)

over a period of 5 min. The ice-bath was then removed and the reaction mixture stirred at room temperature overnight. Excess of reducing agent was destroyed by cautious addition of wet ether followed by saturated aqueous sodium sulphate. After decantation of the ether layer, the reaction mixture was thoroughly extracted with ethyl acetate. The combined organic extracts were dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated to give a mushy white solid. Trituration of this material with a small volume of light petroleum-ether (1:1) gave the *diol* (**8**) *monohydrate* (0.62 g, 41%). The filtrate was evaporated and the residue triturated with a small volume of acetonitrile to give a further solid which

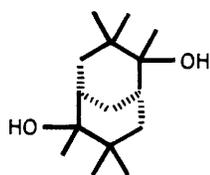


Figure 3. The structure of 2,6-dihydroxy-2,3,3,6,7,7-hexamethylbicyclo[3.3.1]nonane (**8**) emphasising its similarity to two pentamethyl-ethanol units

was filtered to give the diol (**9**) (0.44 g, 31%). The relative proportions of these two diol products were noted to vary from one reaction to the next, for reasons which are not known.

*exo-2,exo-6-Dihydroxy-2,3,3,6,7,7-hexamethylbicyclo[3.3.1]nonane monohydrate (8)*. M.p. 149.5–150.0 °C (from ethyl acetate) (Found: C, 69.9, H, 11.8.  $C_{15}H_{28}O_2 \cdot H_2O$  requires C, 69.7; H, 11.7%);  $m/z$  (chemical ionisation m.s. with pyridine and hydrogen): 320.2629  $[(M + H + \text{pyridine})^+]$ ;  $C_{20}H_{34}NO_2$  requires 320.2589, 302.2536  $\{[(M - 18) + H + \text{pyridine}]^+\}$ ;  $C_{20}H_{32}NO$  requires 302.2483;  $m/z$  (electron impact m.s.,  $\geq 10\%$ , plus significant peaks) 240 ( $M^+$ , trace %), 222 (7), 204 (4), 189 (7), 181 (38), 166 (42), 151 (15), 137 (17), 123 (37), 121 (25), 119 (10), 109 (17), 107 (38), 97 (10), 96 (11), 95 (35), 93 (13), 86 (71), 83 (20), 82 (24), 81 (18), 71 (34), 69 (15), 67 (15), 59 (10), 57 (22), 55 (20), 43 (100), 41 (34), and 40 (20);  $\nu_{\max}$  (paraffin mull) 3 350s, 1 140w, 1 090s, 1 070m, 1 020w, 945w, and 915m  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}[(\text{CD}_3)_2\text{SO}]$  3.82 (s, 2 H, OH, exchanged with  $\text{D}_2\text{O}$ ), 3.36 (s,  $\text{H}_2\text{O}$ , exchanged with  $\text{D}_2\text{O}$ ), 1.9–1.5 (m, 4 H), 1.4–1.0 (m, 4 H), 1.07 (s, 6 H), 0.99 (s, 6 H), and 0.87 (s, 6 H);  $\delta_{\text{C}}(\text{CDCl}_3)$  76.4(s), 42.7(d), 39.1(t), 36.9(s), 30.3(q), 29.8(q), 25.5(q), and 19.2(t). This material was recrystallised from ethyl acetate, diethyl ether, acetonitrile, methanol, carbon tetrachloride and tetrahydrofuran with retention of water and without any indication (i.r.) of organic solvent incorporation. Crystals for X-ray analysis were grown from acetonitrile–light petroleum (b.p. 60–80 °C) by evaporation.

*exo-2-Hydroxy,exo-6-hydroxymethyl-2,3,3,7,7-pentamethylbicyclo[3.3.1]nonane (9)*. M.p. 181–182 °C (from ethyl acetate) (Found: C, 75.0; H, 11.9.  $C_{15}H_{28}O_2$  requires C, 74.95; H, 11.7%);  $\nu_{\max}$  (paraffin mull) 3 380s, 1 110s, 1 080s, 1 040m, 1 025s, 1 010m, 970m, 935w, 905m, and 870w  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}[(\text{CD}_3)_2\text{SO}]$  4.29 (t,  $J$  4.9 Hz, 1 H, exchanged with  $\text{D}_2\text{O}$ ), 3.66 (s, 1 H, exchanged with  $\text{D}_2\text{O}$ ), 3.52–3.48 (m, 1 H, collapsed to dd after exchange,  $\text{CH}_A\text{H}_B\text{OH}$ ), 3.10 (dt, 1 H, collapsed to t after exchange,  $\text{CH}_A\text{H}_B\text{OH}$ ), 1.85–1.83 (m, 1 H), 1.71–1.62 (m, 6 H), 1.50–1.45 (m, 1 H), 1.20–1.17 (m, 1 H), 1.07 (s, 3 H), 1.05 (s, 3 H), 0.98 (s, 3 H), 0.93 (s, 3 H), and 0.82 (s, 3 H);  $\delta_{\text{C}}(\text{CDCl}_3)$  76.5(s), 66.3(t), 47.9(d), 46.0(t), 39.9(d), 39.5(t), 36.8(s), 33.8(q), 31.8(d), 30.3(s), 29.3(q), 29.1(q), 28.6(q), 23.7(q), and 22.7(t).

*X-Ray Crystallographic Determination.*—Crystal data.  $C_{15}H_{28}O_2 \cdot H_2O$ ;  $M = 258.4$ ; triclinic  $P\bar{1}$ ;  $a = 7.388(2)$ ;  $b = 9.292(2)$ ;  $c = 11.466(2)$  Å;  $\alpha = 80.52(2)$ ,  $\beta = 89.68(1)$ ,  $\gamma = 70.85(2)$ °;  $V = 732.4(3)$  Å<sup>3</sup>;  $\mu = 5.90$   $\text{cm}^{-1}$ ;  $Z = 2$ ;  $D_c = 1.17$  g  $\text{cm}^{-3}$ ; 2 165 observed ( $\text{Cu-K}\alpha$ ) reflections;  $2\theta_{\max} = 140$ °;  $R(R_w)$  0.049 (0.072) for C, O anisotropic, H in map locations with isotropic  $B$  equivalent to that of the atom to which it is bound; extinction parameter  $5.5 \times 10^{-4}$ .

*Data collection, processing, and refinement of (8) monohydrate.* 2 769 Independent reflections were recorded using an Enraf-Nonius CAD-4 diffractometer in  $\theta/2\theta$  scan mode using Ni-

filtered Cu radiation ( $\lambda = 1.54056$  Å). Data were corrected for absorption. The procedures used for data collection and processing have been described previously.<sup>14</sup> 2 165 Reflections with  $I/\sigma(I) > 3$  were considered observed. The structure was solved by direct methods (MULTAN 80). Hydrogen atoms were included in positions from a difference Fourier, but not refined. Each was assigned an isotropic temperature factor equivalent to that of the atoms to which it was bonded. Carbon and oxygen atoms were refined with anisotropic thermal parameters. A correction for extinction was applied. Reflection weights used were  $1/\sigma^2(F_o)$  with  $\sigma(F_o)$  being derived from  $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{1/2}$ . Atomic scattering factors and anomalous dispersion corrections were from International Tables for X-Ray Crystallography. Refinement used BLOCKLS, a local version of ORFLS.

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