The Syntheses and Crystal Structures of *exo*-2,*exo*-6-Dihydroxybicyclo-[3.3.1]nonane and *exo*-2,*exo*-6-Dihydroxy-2,6-diethylbicyclo[3.3.1]-nonane which do not contain the Host Helical Canals of Crystalline *exo*-2,*exo*-6-Dihydroxy-2,6-dimethylbicyclo[3.3.1]nonane

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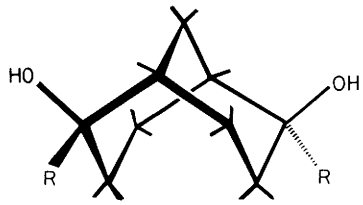
In an attempt to modify the dimensions of the hydrogen-bonded helical canal host structure of crystalline *exo*-2,*exo*-6-dihydroxy-2,6-dimethylbicyclo[3.3.1]nonane (2), the title compounds which involve a minor substituent change at the 2,6 positions were synthesised. Crystals of *exo*-2,*exo*-6-dihydroxybicyclo[3.3.1]nonane (1) and *exo*-2,*exo*-6-dihydroxy-2,6-diethylbicyclo[3.3.1]nonane (3) represent two fully hydrogen-bonded structure types distinctly different from the canal structure of (2) and from each other. Stereochemical analysis has not revealed any significant correlation of crystal structure with molecular structure in these compounds: crystal data, (1) $P2_1/c$, *a* 1 297.0(2), *b* 1 359.1(2), *c* 1 115.0(2) pm, β 118.68(2)°, *Z* 8(×$C_9H_{16}O_2$), *R* 0.046 (3 049 data); (3) *Fdd*2, *a* 1 275.6(2), *b* 1 666.1(2), *c* 2 326.6(3) pm, *Z* 16(×$C_{13}H_{24}O_2$), *R* 0.050 (1 083 data).

CRYSTALS of the bicyclic diol *exo*-2,*exo*-6-dihydroxy-2,6-dimethylbicyclo[3.3.1]nonane (2) contain open helical canals which can include various guest molecules such as chloroform, toluene, dioxan, or acetone without substantial change in crystal structure.[1] In the case of the



(1) R = H
(2) R = CH_3
(3) R = CH_2CH_3

inclusion complex (2E) of (2) with ethyl acetate [(2E) ≡ $(2)_3 \cdot CH_3COOC_2H_5$] the guest molecule is disordered and mobile.[1] The canals in this crystal structure type, shown in Figure 1, have an approximately triangular cross-section (side *ca.* 630 pm) and are a consequence of tight spiral spines of hydrogen bonds, · · · OH · · · OH · · · OH · · ·, between diol molecules. Both the canals and the spines surround crystallographic threefold screw axes in the space-group $P3_121$ (or its enantiomorph). The diol molecules radiate from and interconnect the spines, there being six spines around each canal. Molecules of (2), hydrogen-bonded in the sequence · · · HOC–COH · · · OC–CO · · · HOC–COH · · · OC–CO · · · [where HOC–COH denotes one molecule of (2)] constitute a double helix (pitch 2*c*) around the canals.[1] The host structure type is relatively rigid, m.p. 189—191 °C, and low density (1.10 g cm^{-3}), and yet the canals are lined only with hydrogen atoms of a saturated hydrocarbon.

These compounds may be classified as crystalline multimolecular inclusion compounds with the canal structure type.[2] They are distinct from the better known multimolecular inclusion compounds such as the derivatives of Dianin's compound,[2] and from the *unimolecular* inclusion complexes of canal structure type such as those derived from cyclodextrin.[2]

Spontaneous resolution occurs on crystallisation of (2).[1] We are interested in the generality and utility of the inclusion and resolution which occurs upon crystallisation with the helical canal–spine structure type exhibited by (2). We note that in this structure type there could be a degree of freedom in which variation (mainly reduction) of the pitch of the hydrogen-bonded spine, incurring minor change in hydrogen-bond dimensions, affects (increases) the cross-sectional area of the canal. Accordingly we have synthesised two immediate homologues of (2), namely (1) and (3), in which the 2,6-substituents are one carbon atom smaller and larger respectively than the methyl substituent of (2). Higher-density structures with different hydrogen-bonding networks occur in crystals of (1) and (3), which have not yet been observed to form inclusion complexes or to spontaneously resolve on crystallisation. We have sought stereochemical explanations for these differences.

RESULTS

Synthesis.—The synthetic routes to (1) and (3) are shown in the Scheme. The synthesis of (1) was based on the observation of Schaefer[3] that the *exo*-epoxide of bicyclo-[3.3.1]non-2-ene was reduced in 77% yield to a single alcohol product which was identified as *exo*-2-hydroxybicyclo[3.3.1]nonane. The preparation of the diethyl compound (3) follows the methodology used in the original synthesis of (2).[1]

Crystal Structures.—The measured densities of crystalline (1)—(3) are 1.19, 1.10, and 1.15 g cm^{-3}, respectively. All three crystal structures are fully hydrogen bonded, in that each hydroxy-group engages one donor and one acceptor hydrogen bond, and the density variations therefore reflect differences in packing density.

The three compounds possess different crystallographic symmetry: there are two molecules of (1) per asymmetric unit in the monoclinic space-group $P2_1/c$, half a molecule of

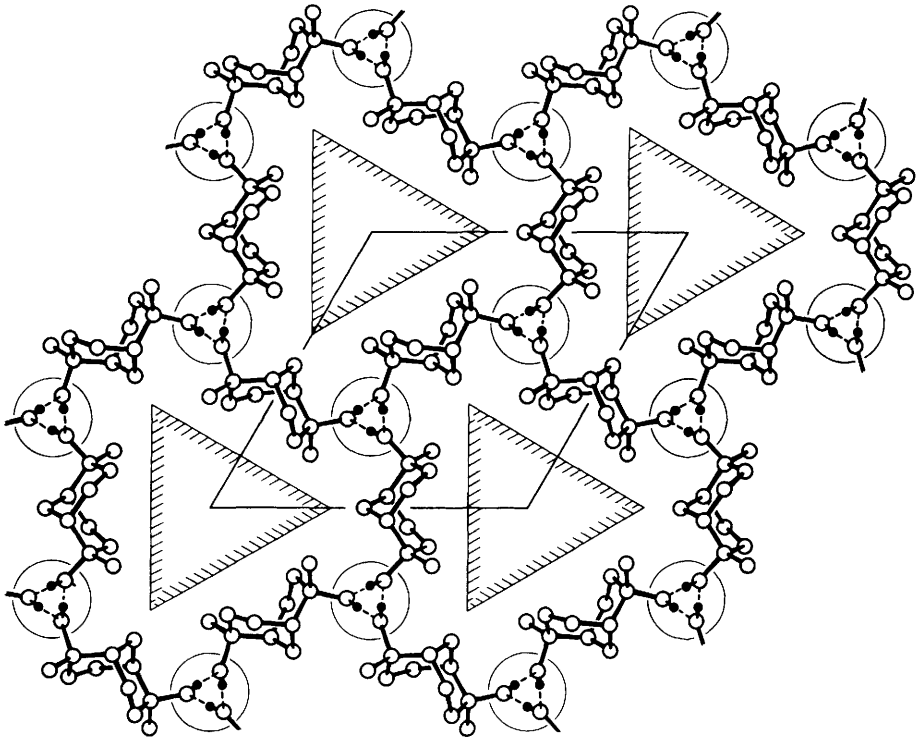


FIGURE 1 Projection view, parallel to the threefold screw axes, of the diol (2) host network: the filled circles and dotted lines represent OH hydrogen atoms and hydrogen bonds respectively. The canals are outlined as triangles, and the hydrogen-bonded spines are circled. Hydrogen atoms are omitted for clarity

(2) per asymmetric unit of the trigonal space-group $P3_121$,* and one molecule of (3) per asymmetric unit of the orthorhombic space-group *Fdd*2. Presentation and comparison of the structures are made with the common atom labelling scheme (I) in which the primes reflect the exact or pseudo C_2 symmetry of the molecule. The two independent molecules of (1) are postscripted A, B. Hydrogen atoms on atom X are labelled HX or H*n*X (n = 1—3). Atomic coordinates are listed in Table 1, and intramolecular dimensions are presented in Table 2.

The *molecular* structures of the three compounds are virtually identical, and not subject to substituent perturbation. Intramolecular dimensions are given in Table 2: the estimated standard deviations (e.s.d.s) for samples of chemically comparable dimensions are generally smaller than the e.s.d.s of individual values. However the crystal structures and hydrogen-bonding networks are distinctly different.

Hydrogen-bonding Networks.—Different aspects of the crystal structure of (1) are shown in Figures 2 and 3. Figure 2, a simplified diagrammatic projection, shows that the molecules are stacked along the *b* direction with a pseudo-hexagonal array of stacks. However there is no similarity with the trigonal stacking of (2) shown in Figure 1, as the molecules of (1) are canted differently with respect to the stacking axis. The angle between the C(3)–O bond and the stacking axis is 54.1, 31.3° in (1) and 102.5° in (2).

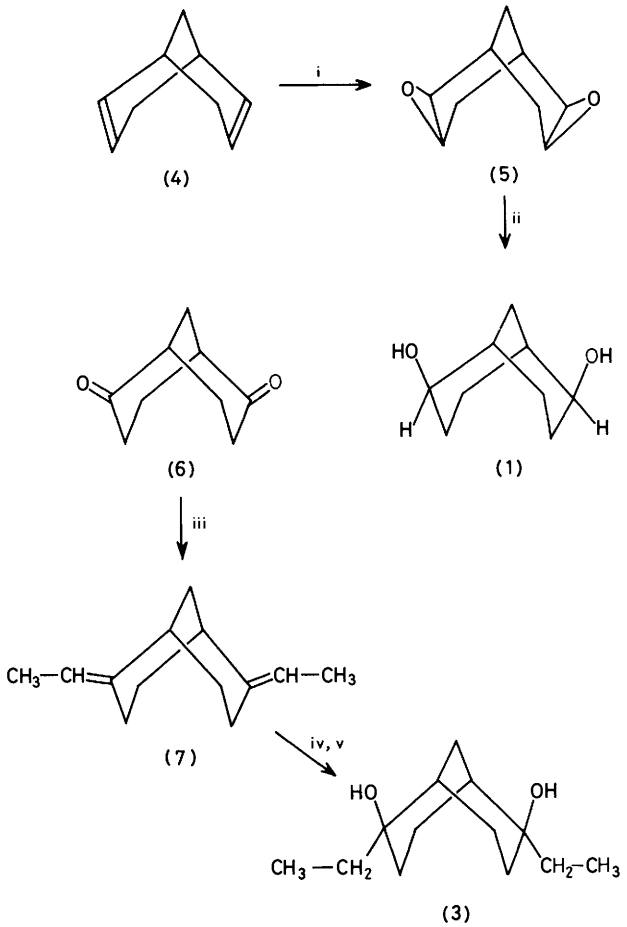
The hydrogen-bonding network in crystalline (1) comprises infinite $\cdots \overset{C}{O}H \cdots \overset{C}{O}H \cdots \overset{C}{O}H \cdots$ connections in which the linkages alternate as inter- and intra-stack, and extension occurs according to the crystal *c*-glide operation. The assemblage of molecules linked along the *c*-direction by the hydrogen-bonding chain is shown in Figure 3, which reveals that this chain loosely approximates to a spiral. However there is no geometrical similarity with the $\cdots \overset{C}{O}H \cdots \overset{C}{O}H \cdots \overset{C}{O}H \cdots$ spirals in crystalline (2).

The crystal structure of (3) is different from the other two in that the $\cdots \overset{C}{O}H \cdots \overset{C}{O}H \cdots \overset{C}{O}H \cdots$ hydrogen-bonding connections occur in four-membered cycles, not infinite chains. As shown in Figure 4 the molecules are stacked along 2_1 screw axes parallel to *c* in space-group *Fdd*2. The hydrogen bonds protrude from these stacks, approximately normal to the 2_1 axes, and provide links between four adjacent stacks arranged around a twofold axis. The oxygen atoms of the hydrogen-bonded rhombus are displaced ±47 pm from their mean plane.

DISCUSSION

The three homologous molecules (1)—(3) crystallise with three quite different crystal structures, each with the maximum number of hydrogen bonds, but with different hydrogen-bonding networks. Two of the crystal structure types, (1) and (3), do not contain voids of volume sufficient for the formation of inclusion complexes, and represent alternatives to the more interesting helical canal structure type (2). The main question that

* The crystal structure of pure (2) has not been determined in detail, but it is known from polycrystalline diffraction measurements to be isostructural with its ethyl acetate inclusion complex (2E). Dimensions quoted are those of (2E).

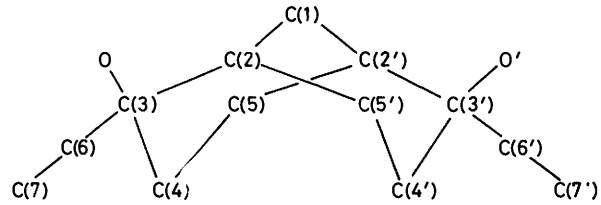


SCHEME *Reagents*: i, *m*-$ClC_6H_4CO_3H$; ii, $LiAlH_4$; iii, $Ph_3P{=}CH{-}CH_3$; iv, $Hg(OAc)_2$; v, $NaBH_4$–NaOH

we raise is why either the slightly smaller (1) or larger (3) molecules did not crystallise with the structure of (2). An alternative consideration is why (2) did not crystallise with the structures of (1) or of (3). There are several possible reasons that should be examined: one is that the 2,6-substituents R influence the directions of hydrogen-bonding relative to the molecular framework; another is that substituents influence the non-bonded intermolecular contacts in the crystal.

In the following analysis the two donor and two acceptor hydrogen bonds engaged by each molecule are denoted as in (II). Table 3 sets out the directions of the C–O, O–H, and O · · · O vectors associated with the hydrogen-bonding in each molecule in structures (1)—(3), referenced to a common molecular cartesian axial system in which X is C(4) ⟶ C(4′), Y is C(2) ⟶ C(2′), and Z passes through C(1). Figure 5 shows these vectors diagrammatically for the four independent molecules in the three crystals.

Looking first at the patterns of hydrogen-bond geometry, it can be seen that there are no significant differences in C–O directions, and that the hydrogen-bonding geometries of the two independent molecules in structure (1) are remarkably similar. However, the main point is that the O–H · · · O_A and O′–H′ · · · O_A′ bonds are approximately perpendicular to the X and Y molecular axes, but different distributions of directions occur in the three structures: in structure (1) O–H · · · O_A is approximately perpendicular to Y while O′–H′ · · · O_A′ is approximately perpendicular to X; in structure (2) both bonds are approximately perpendicular to X; while in structure (3) both bonds are approximately perpendicular to Y.



(I)

There is no apparent systematic influence of substituent R on the hydrogen-bond direction. In both (1) and (3), the extreme members of the series, the hydrogen bond closest to the substituent (that approximately perpendicular to X) bonds away from the substituent in the YZ plane, whereas in (2E) the comparable hydrogen bond is in fact closer to the substituent.

The structures differ in the O_D · · · O · · · O_A and O_D′ · · · O′ · · · O_A′ sector angles. In structure (2E) both angles are large (122.5°), in structure (3) they are both small (81.6, 85.0°), while in structure (1) these angles are distributed more closely around the ideal tetrahedral value. The large hydrogen-bond sector angle appears to be necessary for structure (2): a smaller angle decreases the separation between molecules in the *c*-direction. A significant observation is that the enlarged sector angle in (2E) is effected by an adjustment in the direction of the hydrogen bond (O · · · H–O_D) further from the methyl substituent. Nothing in *molecules* (1) and (3) prevents a similar direction for that hydrogen bond in their crystals. We conclude that the molecular substituent is not influencing crystal structure by directing the hydrogen bonding.

It can be readily shown that a larger diol of the series (1)—(3) could not fit into the crystal structure of a smaller member. Impossible intermolecular steric crowding due to the substituent occurs if molecules (2) or (3) (including rotamerism within the ethyl substituent) are placed in the crystals of (1) or (2), respectively.

A final point of contrast of the structures concerns their chirality. Racemic (2) resolves on crystallisation [1] with a structure containing one enantiomer per crystal, whereas (1) and (3) crystallise as racemates. It is conceivable that resolved (1) or (3) could crystallise with a chiral structure similar to that of (2).

The effects of various modifications to the host molecule on the occurrence of crystalline multimolecular inclusion complexes have been investigated in greatest detail for Dianin's compound, 4-*p*-hydroxyphenyl-2,2,4-trimethylchroman.[2] In most cases the clathrate crystal

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$) for (1) and (3) [a,b]

Atom	Compound (1) x	Compound (1) y	Compound (1) z	Compound (3) x	Compound (3) y	Compound (3) z
C1A	5 426(1)	6 198(1)	8 895(1)	6 575(3)	1 034(2)	0 739(2)
C2A	5 961(1)	6 262(1)	7 946(2)	6 634(2)	0 465(2)	1 254(2)
C3A	5 831(1)	7 298(1)	7 362(2)	7 631(3)	0 621(2)	1 608(2)
C4A	4 581(1)	7 691(1)	6 689(2)	8 613(3)	0 623(2)	1 239(2)
C5A	3 946(2)	7 478(1)	7 527(2)	8 512(3)	1 044(2)	0 657(2)
C6A				7 761(4)	0 024(2)	2 107(2)
C7A				6 892(5)	0 005(3)	2 544(2)
OA	6 585(1)	7 916(1)	8 485(1)	7 492(3)	1 417(1)	1 842
C2′A	4 116(1)	6 423(1)	8 078(2)	7 490(3)	0 855(2)	0 334(2)
C3′A	3 491(1)	5 641(1)	6 973(2)	7 410(3)	−0 000(2)	0 089(2)
C4′A	4 064(2)	5 465(1)	6 075(2)	7 294(3)	−0 624(2)	0 559(2)
C5′A	5 411(2)	5 458(1)	6 849(2)	6 508(3)	−0 391(2)	1 025(2)
C6′A				8 320(4)	−0 253(3)	−0 312(2)
C7′A				8 458(5)	0 260(4)	−0 836(2)
O′A	3 491(1)	4 720(1)	7 598(1)	6 463(2)	0 004(2)	−0 253(2)
HOA	6 496(24)	8 474(21)	8 205(28)	8 004	1 789	1 982
HO′A	2 920(23)	4 809(18)	7 814(28)	5 958	−0 368	−0 392
C1B	10 309(1)	6 158(1)	6 603(2)			
C2B	11 051(1)	6 148(1)	8 161(2)			
C3B	11 078(1)	5 110(1)	8 704(2)			
C4B	9 866(1)	4 672(1)	8 230(2)			
C5B	9 029(1)	4 846(1)	6 716(2)			
OB	11 736(1)	4 510(1)	8 253(1)			
C2′B	9 055(1)	5 890(1)	6 220(1)			
C3′B	8 527(1)	6 671(1)	6 755(2)			
C4′B	9 263(2)	6 894(1)	8 260(2)			
C5′B	10 582(2)	6 935(1)	8 761(2)			
O′B	8 361(1)	7 576(1)	6 013(1)			
HOB	11 664(23)	3 891(21)	8 452(31)			
HO′B	7 882(24)	7 486(17)	5 265(27)			

[a] Estimated standard deviations in parentheses. [b] Excluding calculated co-ordinates for hydrogen atoms bonded to carbon.

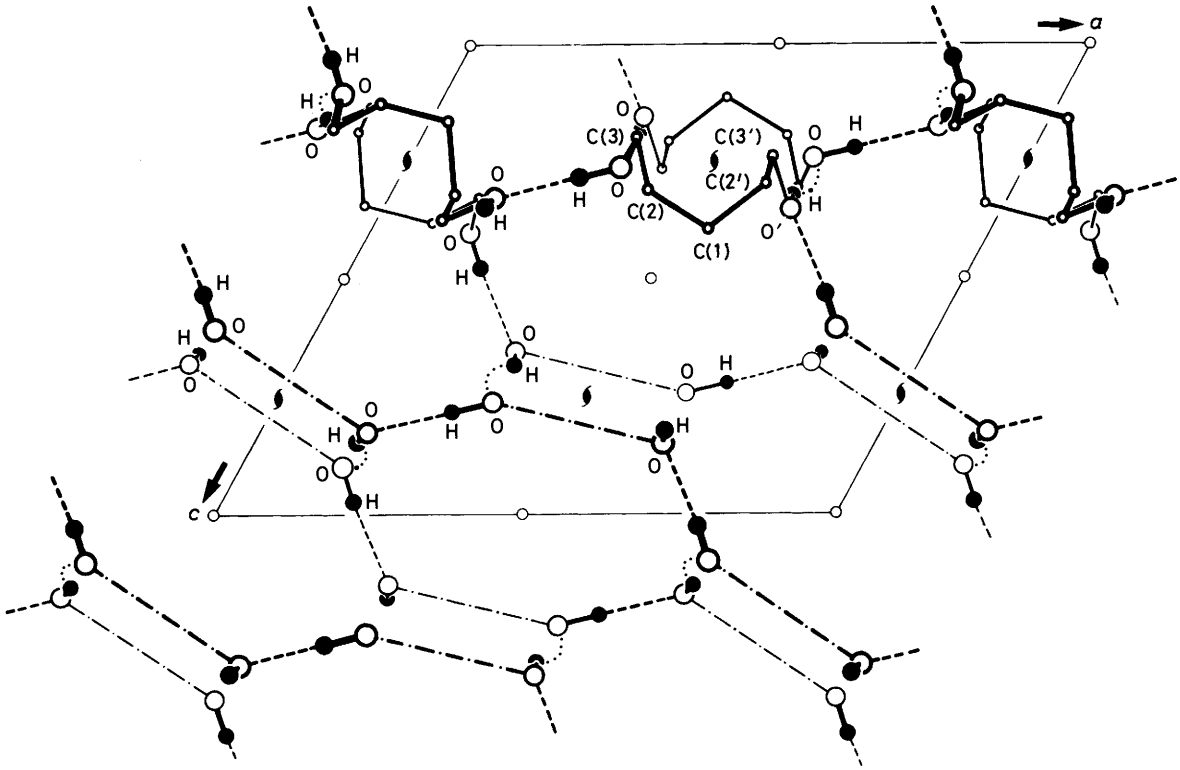


FIGURE 2 Diagrammatic representation of the crystal structure of (1), projected along *b*, to show the stacking of molecules along the twofold screw axes. Molecules in the upper row of stacks (*z ca.* ¼) are represented only by the atom sequence HO–C(3)–C(2)–C(1)–C(2′)–C(3′)–O′H′, while the remaining molecules are symbolised simply as HO—·—·—·O′H′. The broken lines represent hydrogen bonds between stacks, while hydrogen bonds along the stacks are marked as dotted curves, for clarity

structure is maintained, but in a small proportion of instances a different crystal structure occurs, with a more closely packed arrangement of hydrogen bonds.

Conclusions.—The attempted modification of the dimensions of the hydrogen-bonded helical canal structure of (2) through decrease or increase of the 2,6-substituents by one carbon atom has not been successful. Other fully hydrogen-bonded crystal structures form instead. Although the minor changes in molecular size are sufficient to change the type rather than the dimensions of crystal structure, no direct *molecular* determinant of the hydrogen-bonding geometry in the crystal can be identified. It is concluded that the crystal structures of (2), and of (1) and (3), represent relatively shallow wells on the crystal structure–free energy surface for these compounds.

TABLE 2

Comparison of intramolecular dimensions (pm, degree) of compounds (1)—(3) [a]

Dimension	(1) [b]	(2)	(3)	Mean [sample size] [c]	Sample e.s.d.
C1–C2	152.2(2), 153.0(2)	153.2(3)	152.9(5)	152.6 [7]	0.6
C1–C2′	152.5(2), 151.4(2)		153.0(5)		
C2–C3	152.6(2), 153.0(2)	154.5(4)	153.8(4)	153.4 [7]	0.6
C2′–C3′	153.2(2), 153.1(2)		153.8(5)		
C3–C4	151.9(2), 151.9(2)	152.6(4)	151.8(5)	151.9 [7]	0.5
C3′–C4′	152.5(2), 151.0(2)		151.6(5)		
C4–C5	154.1(3), 152.6(2)	152.6(4)	153.0(5)	152.9 [7]	0.6
C4′–C5′	153.3(3), 152.4(3)		152.6(5)		
C5–C2′	153.3(2), 152.9(2)	153.0(4)	153.8(5)	153.3 [7]	0.3
C5′–C2	153.6(2), 153.4(3)		153.1(5)		
C3–O	143.3(2), 143.3(2)	145.3(3)	144.5(4)	144.1 [7]	0.8
C3′–O′	143.3(2), 144.0(2)		144.7(4)		
C3–C6		152.2(4)	153.7(5)	153.5 [3]	1.3
C3′–C6′			154.7(6)		
C6–C7			150.4(7)		
C6′–C7′			149.9(7)		
O–HO	81(3), 89(3)	92(2)	96	88 [7]	7
O′–HO′	89(3), 77(3)		95		
C2–C1–C2′	108.8(1), 108.9(1)	108.7(3)	108.9(3)	108.8 [4]	0.1
C1–C2–C3	110.8(1), 109.9(1)	110.0(2)	110.9(3)	110.5 [7]	0.4
C1–C2′–C3′	110.4(1), 110.1(1)		111.0(3)		
C1–C2–C5′	108.7(1), 108.9(1)	108.1(2)	107.5(3)	108.6 [7]	0.7
C1–C2′–C5	109.4(1), 109.2(1)		107.8(3)		
C3–C2–C5′	113.8(1), 114.1(1)	116.3(2)	115.3(3)	114.8 [7]	0.9
C3′–C2′–C5	114.1(1), 114.2(1)		115.3(3)		
C2–C3–C4	114.1(1), 113.6(1)	112.2(2)	112.3(3)	113.1 [7]	0.9
C2′–C3′–C4′	113.6(1), 114.2(1)		112.0(3)		
C2–C3–O	106.2(1), 106.9(1)	107.9(2)	104.8(2)	107.2 [7]	2.1
C2′–C3′–O′	109.8(1), 109.8(1)		104.8(3)		
C4–C3–O	110.2(1), 110.2(1)	105.5(2)	108.2(3)	108.2 [7]	1.7
C4′–C3′–O′	107.2(1), 107.9(1)		108.5(3)		
C3–C4–C5	112.9(1), 113.1(1)	114.2(2)	115.6(3)	114.1 [7]	0.9
C3′–C4′–C5′	114.5(1), 114.5(2)		113.7(3)		
C4–C5–C2′	113.7(1), 114.6(1)	114.9(2)	114.2(3)	114.5 [7]	0.5
C4′–C5′–C2	114.3(1), 115.2(1)		114.6(3)		
C4–C3–C6		110.7(2)	109.9(3)	109.8 [3]	1.0
C4′–C3′–C6′			108.8(3)		
C2–C3–C6		112.9(2)	112.7(3)	113.6 [3]	1.4
C2′–C3′–C6′			115.2(3)		
O–C3–C6		107.3(2)	108.8(3)	107.8 [3]	0.9
O′–C3′–C6′			107.2(3)		
C3–C6–C7			116.4(3)		
C3′–C6′–C7′			115.0(4)		
C3–O–HO	108(2), 108(2)	109	130		
C3′–O′–HO′	102(2), 108(2)		138		

[a] Values are those of molecule (2) in the crystal of (2E), its ethyl acetate inclusion complex. [b] Entries are for molecules A,B. [c] The sampling assumes equivalence of the four molecules in the three crystals, and C_2 effective molecular symmetry.

EXPERIMENTAL

^{1}H and ^{13}C n.m.r. spectra were recorded using a JEOL FX-100 spectrometer and are reported as chemical shifts (δ) relative to internal $SiMe_4$. The substitution of carbon atoms was determined by off-resonance decoupling. I.r. spectra were recorded using a Perkin-Elmer SP 1000 spectrometer. M.p.s were recorded on a Kofler instrument and are uncorrected.

Bicyclo[3.3.1]*nona*-2,6-*diene* (4).—Bicyclo[3.3.1]nonane-2,6-diol [4] (6.24 g, 0.04 mol) (prepared by lithium aluminium hydride reduction of the diketone [5]) in dry pyridine (40 ml) was allowed to react with toluene-*p*-sulphonyl chloride (17 g) in dry pyridine (40 ml) at 0 °C. After two days at this temperature the mixture was worked up by extraction with chloroform and aqueous copper sulphate. The pyridine-free chloroform extracts were dried (Na_2SO_4) and solvent evaporated to give the 2,6-ditosylate as a solid. The crude

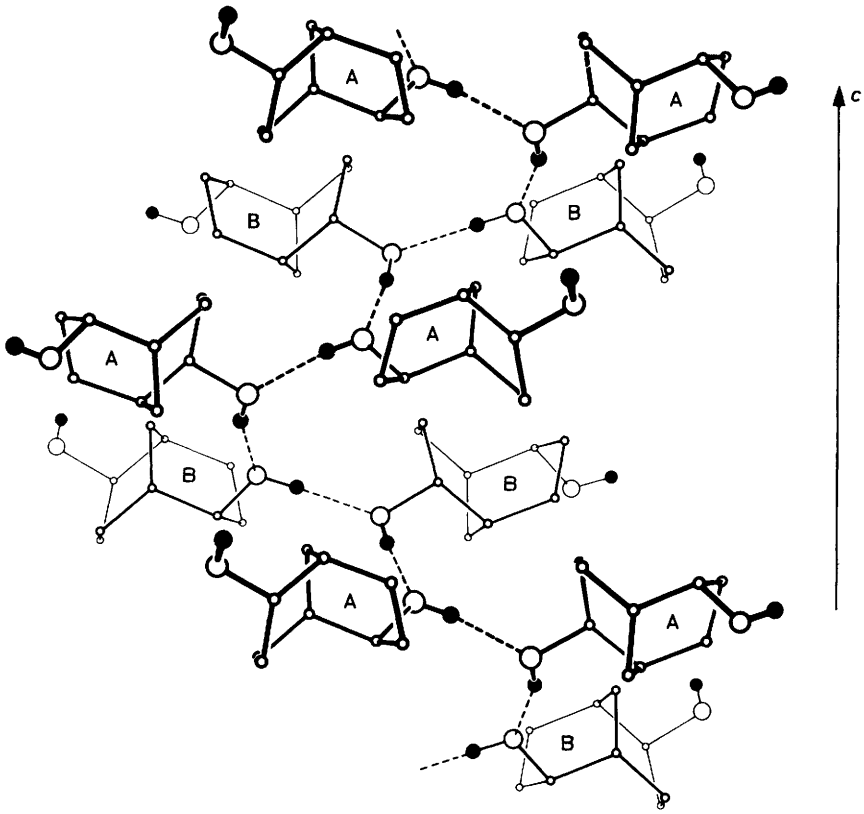


FIGURE 3 The infinite hydrogen-bonded linkage of molecules in crystalline (1)

tosylate was placed in a small-scale distillation apparatus with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) (15 ml) and the mixture warmed with a microburner to drive off volatile material distilling over 100—200 °C. A black solid residue was left in the flask. The distillate was mixed with ether and washed with 2M-HCl, saturated $NaHCO_3$, and then the ethereal solution dried (Na_2CO_3). Ether was distilled off to give a clear oil which was eluted through a short column of neutral alumina with pentane. This solution was distilled to give solvent, then bicyclo[3.3.1]nona-2,6-diene [4,6] over 150—165 °C (3.83 g, 80%).

exo-2,3-exo-6,7-*Diepoxybicyclo*[3.3.1]*nonane* (5).—*m*-Chloroperbenzoic acid (12.08 g of 80% purity, 0.056 mol) was stirred at 0 °C in chloroform (dried over anhydrous $CaCl_2$) (100 ml) and bicyclo[3.3.1]nona-2,6-diene (3.00 g, 0.025 mol) in dry $CHCl_3$ (15 ml) was added. After a few minutes the reaction mixture turned nearly solid. Stirring was continued overnight and 10% aqueous sodium sulphide added till a blue colouration was no longer given with starch–KI paper. The mixture was then extracted with aqueous sodium hydrogencarbonate. The chloroform extract was washed again with $NaHCO_3$, with water, and then dried (Na_2SO_4). Solvent was evaporated from the filtrate to give an oil, which was eluted through a short column of neutral alumina with light petrol : ether (2 : 1) (250 ml). Evaporation of solvent gave the *diepoxide* (2.62 g, 69%) as a solid. Recrystallisation from pentane gave m.p. 173—174 °C (Found: C, 70.6; H, 7.9. $C_9H_{12}O_2$ requires C, 71.0; H, 7.95%), $\nu_{max.}$ (paraffin mull) 985(s), 925(s), 870(s), 820(s), and 770(s) cm^{-1}, δ_H ($CDCl_3$) 1.42—1.45 (m, 2 H), 1.78—2.30 (m, 6 H), 2.91—2.93 (m, 2 H), and 2.95—3.18 (m, 2 H).

exo-2,exo-6-*Dihydroxybicyclo*[3.3.1]*nonane* (1).—Diepoxide (2.83 g, 18.6 mmol) in ether (15 ml) was added to a stirred solution of lithium aluminium hydride (2.8 g, 74 mmol) in ether (30 ml) at a rate to maintain steady reflux. The mixture was then stirred at room temperature for 3 d. Excess of $LiAlH_4$ was destroyed by addition of saturated sodium sulphate, the ether was evaporated, water added, and the aqueous solution continuously extracted with ethyl acetate for 2 d. Evaporation of solvent gave the *diol* (2.18 g, 75%) as a solid. Recrystallisation from ethyl acetate gave m.p. 204—206 °C (Found: C, 69.5; H, 10.3. $C_9H_{16}O_2$ requires C, 69.2; H, 10.3%), $\nu_{max.}$ (paraffin mull) 3 460(s), 1 025(s), 995(s), 980(s), 955(m), 930(s), and 895(m) cm^{-1}, δ_H([$^2H_6$]DMSO) 1.26—1.86 (m, 12 H), 3.64 (s, $W_{1/2}$ 8 Hz, 2 H), and 4.29 and 4.33 (d, J 3.2 Hz, 2 H, exchanged with D_2O). The value of $W_{1/2}$ for the C(2)–C(6) methine is typical of that expected for a bicylo[3.3.1]nonane derivative with *exo*-C(2)–C(6) substituents and existing in the twin-chair conformation,[7] δ_C ([$^2H_6$]DMSO) 20.8, 23.3 and 28.4 (all t, CH_2), 34.3 [d, C(1)–C(5)] and 69.3 [d, C(2)–C(6)].

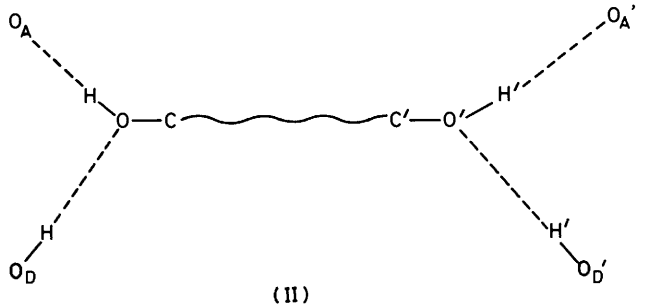
Samples of the diol recrystallised from ethyl acetate or tetrahydrofuran exhibited identical i.r. spectra with no indication of solvent inclusion.

The crystals for *X*-ray study were recrystallised from tetrahydrofuran.

2,6-*Diethylidenebicyclo*[3.3.1]*nonane* (7).—A solution of ethyltriphenylphosphonium bromide (22.28 g, 0.06 mol) in dry DMSO (60 ml) was stirred under nitrogen and a solution of sodium methylsulphinylmethylide [8] (0.06 mol) in DMSO added by syringe. After 10 min, bicyclo[3.3.1]nonane-2,6-dione [5] (6) (4.56 g, 0.03 mol) was added as a powder, residual

traces of material being washed into the mixture with dry DMSO (20 ml). The deep red solution turned darker and warmed up.

After 10 min stirring, the mixture was heated to 70 °C and stirred at this temperature for 2 h. The cooled mixture was worked up with water and pentane in the usual manner.[8] The combined pentane extracts were dried (anhydrous Na_2CO_3), then the filtrate distilled down to a volume of *ca.* 10 ml. This concentrated solution was eluted through a



(II)

column of activated, neutral alumina with pentane (500 ml) and solvent distilled off to give the diene [9] as an oil (2.08 g, 39.3%), $\nu_{max.}$ (film) 1 660(w) and 810(s) cm^{-1}.

The material on the column was further eluted with 50% ether–pentane (500 ml). Removal of solvent by distillation gave 6-*ethylidenebicyclo*[3.3.1]*nonane*-2-*one* (0.90 g, 18.3%) as an oil, $\nu_{max.}$ film 1 715(s), 1 665(w), and 810(m) cm^{-1}.

exo-2,exo-6-*Dihydroxy*-2,6-*diethylbicyclo*[3.3.1]*nonane* (3). —Mercury(II) acetate (7.52 g, 23.6 mmol) was stirred in water (40 ml) and purified tetrahydrofuran (THF) (40 ml, freshly distilled from lithium aluminium hydride to remove peroxides), then a solution of 2,6-diethylidenebicyclo[3.3.1]-nonane (2.08 g, 11.8 mmol) added as a solution in purified THF (10 ml). The yellow colour [10,11] faded after *ca.* 40 min, but stirring was continued for a total of 2.5 h, before addition of 3M aqueous sodium hydroxide (25 ml), quickly followed by 3M aqueous sodium hydroxide–0.5M-sodium borohydride (25 ml). THF was evaporated under reduced pressure and then the aqueous solution continuously extracted with ethyl acetate for 4 d.

Evaporation of solvent gave a gummy solid which was heated with ethyl acetate (150 ml) and filtered. The filtrate was concentrated to 100 ml and re-filtered. Both samples of filtered solid were identical and inorganic (H_3BO_3). Evaporation of solvent from the filtrate gave a gummy solid which was triturated with carbon tetrachloride (10 ml) and the solid *diol* (1.12 g, 45%) filtered and dried, m.p. 168—170 °C (from ethyl acetate) (Found: C, 73.6; H, 11.2. $C_{13}H_{24}O_2$ requires C, 73.5; H, 11.4%), $\nu_{max.}$ (paraffin mull) 3 400(s), 1 195(m), 1 085(m), 975(s), and 920(s) cm^{-1}, δ_H ([$^2H_6$]DMSO) 0.80 (t, *J* 7 Hz, 6 H, CH_3), 1.20—1.85 (complex m, 16 H), 3.65 (s, 2 H, exchanged with D_2O), δ_C

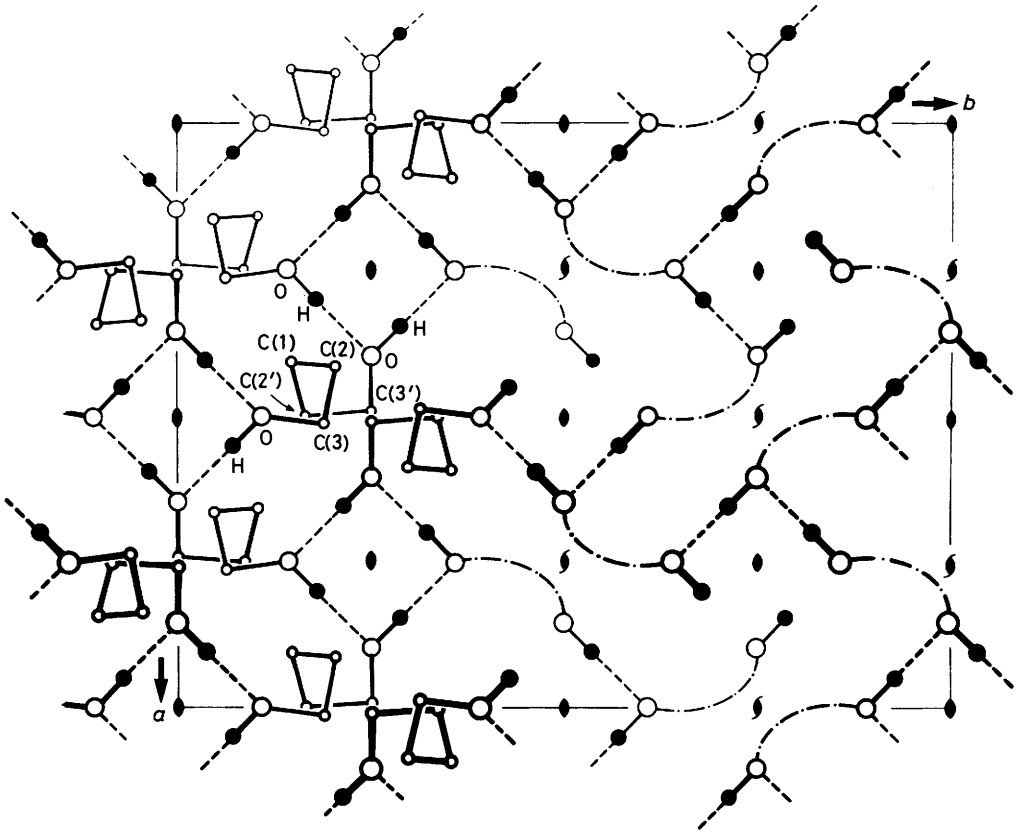


FIGURE 4 Diagrammatic representation of the crystal structure of (3), projected along *c*, to show the cyclic hydrogen bonding in relation to crystallographic twofold rotation (♦) and twofold screw (𝍐) axes. Molecules on the left side of the figure are represented only by the atom connection HO–C(3)–C(2)–C(1)–C(2′)–C(3′)–O′H′, while those on the right side are symbolised simply as HO— · — · —O′H′

([$^2H_6$]DMSO) 6.5 (q, CH_3), 23.2, 25.4, 33.3, and 33.5 (all t, CH_2), 36.3 [d, C(1)–C(5)], and 71.4 [s, C(2)–C(6)].

Samples of the diol recrystallised from ethyl acetate, acetonitrile, or acetone exhibited identical i.r. spectra with no indication of solvent inclusion.

TABLE 3

Angles between vectors associated with hydrogen-bonding[a] and the molecular cartesian axes

Vector	Molecule (1)A	(1)B	(2E)[b]	(3)
C–O	138,[c] 99,[c] 50[c]	138, 99, 50	139, 94, 50	138, 97, 48
C′–O′	37, 80, 54	38, 80, 54	41, 86, 50	43, 85, 47
O–H	149, 88, 121	149, 83, 120	84, 146, 57	167, 78, 95
O′–H′	94, 11, 80	95, 22, 69	96, 34, 57	13, 102, 85
O–O_A	145, 96, 124	150, 86, 120	95, 149, 60	167, 79, 95
O–O_D	89, 109, 19	99, 116, 28	145, 55, 87	104, 114, 29
O′–O_A′	81, 16, 77	99, 18, 74	95, 31, 60	12, 101, 86
O′–O_D′	20, 107, 101	15, 103, 97	35, 125, 87	84, 81, 11

[a] The vector notation and the molecular X, Y, Z axis definitions are shown in Figure 5. [b] The ethyl acetate inclusion complex of (2). [c] The three angles (degrees) are with the X, Y, and Z axes respectively.

The crystals for X-ray study were recrystallised from acetonitrile.

Crystallography.—Numerical details of the crystals, the X-ray diffractometry, and the structure refinement are given in Table 4. Space-groups were determined photographically, and intensity data were measured with a Siemens diffractometer and processed as previously described.[12] Calculated corrections for absorption were applied. Scattering factors, including corrections for anomalous scattering by oxygen, were from International Tables.[13] Larson's [14] isotopic extinction correction was included and refined in both structures. Least-squares refinement minimized $\Sigma w|\Delta F|^2$, with $w = [\sigma(F_o)]^{-2}$.

Structure (1). All non-hydrogen atoms were located by direct methods (MULTAN 74). Hydroxy hydrogen atoms were located on a difference map after refinement of non-hydrogen atoms, while hydrocarbon hydrogen atoms were included at ideal positions. In the final full matrix least-squares refinement all positions except those of the hydrocarbon hydrogen atoms were varied, as were anisotropic temperature factors for all non-hydrogen atoms. The hydrogen-atom temperature factors were maintained equal to those of their bonded atoms. A final difference electron density map showed no features greater than 0.23×10^3 e nm^{-3}.

Structure (3). Structure solution by MULTAN 80 revealed all but one oxygen atom, which was subsequently located by Fourier synthesis. After refinement of the non-hydrogen atoms (anisotropic temperature factors) using data at $\sin\theta/\lambda > 0.3$, a difference map confirmed a staggered conformation for the hydrogen atoms of the methyl group. All hydrocarbon hydrogen atoms were included at calculated positions, and assigned temperature factors equal to those of

TABLE 4

Crystallographic details for (1) and (3)

	(1)	(3)
Formula, formula mass	$C_9H_{16}O_2$, 156.2	$C_{13}H_{24}O_2$, 212.3
Crystal description	{100}{110}{101}{011}	{011}{111}{012}{001}
Space-group	$P2_1/c$	$Fdd2$
a/pm	1 297.0(2)	1 275.6(2)
b/pm	1 359.1(2)	1 666.1(2)
c/pm	1 115.0(2)	2 326.6(3)
β/(°)	118.68(2)	
V/nm^3	1.724(1)	4.945(2)
T/°C	21	21
d_{obs}/g cm^{-3}	1.19(1)	1.15(1)
Z	8	16
d_{cal}/g cm^{-3}	1.203	1.140
Radiation, λ/pm	Cu-K_α, 1 54.18	Cu-K_α, 1 54.18
μ/cm^{-1}	6.28	5.49
Min and max values for tramsmission factor	0.687/0.866	0.831/0.919
Crystal dimensions/mm	0.26 × 0.35 × 0.61	0.2 × 0.3 × 0.3
Scan mode	$\theta/2\theta$	$\theta/2\theta$
$2\theta_{max.}$/(°)	140	140
No. of intensity measurements	3 417	1 209
Criteria for observed reflection	$I/\sigma(I) > 2.58$	$I/\sigma(I) > 2.58$
No. of independent observed reflections	3 049	1 083
No. (m) of reflections in final refinement	3 049	1 083
No. of variables refined (n)	212	136
R	0.046	0.050
R_w	0.087	0.070
$[\Sigma^m w\|\Delta F\|^2/(m-n)]^{\frac{1}{2}}$	3.5	2.5
Extinction parameter, g	118(30) × 10^{-6}	91(25) × 10^{-6}

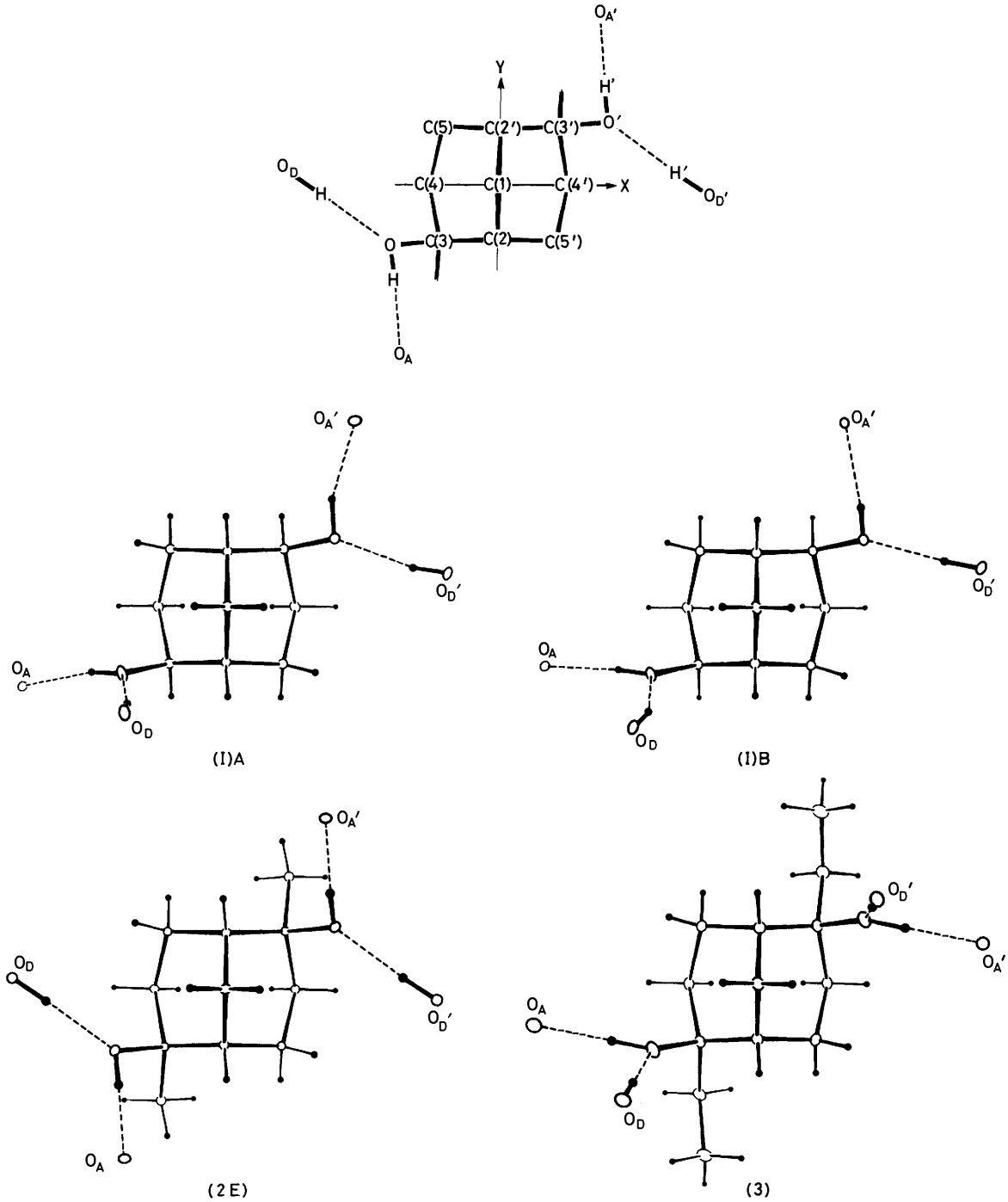


FIGURE 5 Hydrogen-bonding directions relative to the defined *molecular* cartesian axes, for molecules (1)A, (1)B, (2E), and (3)

their bonded atoms. After further refinement to R 0.052, peaks attributable to the hydroxy hydrogen atoms appeared on a difference synthesis, but at positions too close (39, 52 pm) to the oxygen atoms. The hydroxy hydrogen atom positions were idealised, and were not refined. The final refinement model included positional and anisotropic thermal parameters for the non-hydrogen atoms, and an isotropic extinction correction.

Tabulations of atom temperature factors, and listings of observed and calculated structure factors, are included in Supplementary Publication No. SUP 23328 (27 pp).*

* For details of Supplementary Publications see Notices to Authors No. 7, in *J. Chem. Soc., Perkin Trans. 2*, 1981, Index Issue.

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