

## The Synthesis, Infrared Spectra, and Crystal Structures of Three Isomeric Dicyclohexano-14-crown-4 Diols

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From the hydrogenation of the *cis*-dihydroxydibenzo-14-crown-4 (I), three isomeric dicyclohexano-14-crown-4 diols were isolated and separated by fractional crystallisation. *X*-Ray crystal structure analyses established the relative configurations † of: isomer (A), m.p. 134 °C, as (*cis*-1,6,9,20-*trans*-12,17)-9,20-dihydroxy-7,11,18,22-tetraoxatricyclo[16.4.0.0<sup>12,17</sup>]docosane; isomer (B), m.p. 118 °C, as (*cis*-1,6,9,12,17,20)-9,20-dihydroxy-7,11,18,22-tetraoxatricyclo[16.4.0.0<sup>12,17</sup>]docosane; and isomer (C), m.p. 170 °C, as (*cis*-1,6,12,17-*trans*-9,20)-9,20-dihydroxy-7,11,18,22-tetraoxatricyclo[16.4.0.0<sup>12,17</sup>]docosane. For isomer (B) measurements were also made by neutron diffraction. The hydrogen bonding in each crystalline form correlates well with the i.r. spectra. In isomer (B) one hydroxy hydrogen does not take part in hydrogen bonding, the other gives a bond with an O...O distance of 2.925(2) Å (*X*-ray), or 2.935(10) Å (neutron). In isomers (A) and (C) each hydroxy hydrogen atom may occupy one of two sites yielding disordered hydrogen bonds of the type O-H...O or O...H-O; the O...O distances average 2.822(2) Å in isomer (A) and 2.76(1) Å in isomer (C). The packing is also discussed in relation to the melting points and densities.

The hydrogenation of *cis*-dihydroxydibenzo-14-crown-4, (I), with a ruthenium-alumina catalyst under high pressure of hydrogen gives, as main products, three isomeric dicyclohexano diols, (II), corresponding to *cis*-hydrogenation at the ring junction atoms.<sup>1</sup> The isomers could be separated by fractional crystallisation from non-polar solvents. They have greatly differing melting points, 134 °C for isomer (A), 118 °C for the most soluble isomer (B), and 170 °C for the least soluble isomer (C). Their i.r. spectra are similar except in the hydroxy stretching region where the two higher melting isomers give broad bands; at 3 280 cm<sup>-1</sup> for (C), and at 3 330 cm<sup>-1</sup> for (A). The lowest melting isomer, (B), however, gives two bands in this region; a sharp one at 3 560 cm<sup>-1</sup>, and a broader one at 3 440 cm<sup>-1</sup>, suggesting that one of the hydroxy hydrogen atoms is not a hydrogen bond donor. The fractional crystallisation, which was quite straightforward on the first occasion, has always been more difficult in repeated syntheses.

The crystal structures of all three isomers have been determined by *X*-ray diffraction so that the isomers can be identified and their relation to the corresponding bicyclic molecules, (III),<sup>2,3</sup> explored. Of particular interest is a comparison of the packing and hydrogen bonding of the diols. Isomer (B) gave sufficiently large crystals to allow measurements to be made by neutron diffraction, which has enabled us to determine the hydrogen atom co-ordinates relatively more accurately, and to compare the neutron and *X*-ray structures.

### Results and Discussion

Figure 1 gives the crystallographic numbering scheme of the atoms. The crystal data are in Table 1 and atomic co-ordinates in Tables 2(a)–(c). Figures 2(a)–(c) are stereoviews of each molecule. The four oxygen atoms O(1), O(5), O(12), and O(16) define an approximate plane. Isomer (A) has one cyclohexano

ring on each side of this plane with the two hydroxy groups on the same side as the C(6)–C(11) ring. Isomer (B) has both cyclohexano rings and both hydroxy groups on the same side, while isomer (C) has both cyclohexano rings on one side and the hydroxy groups on the other.

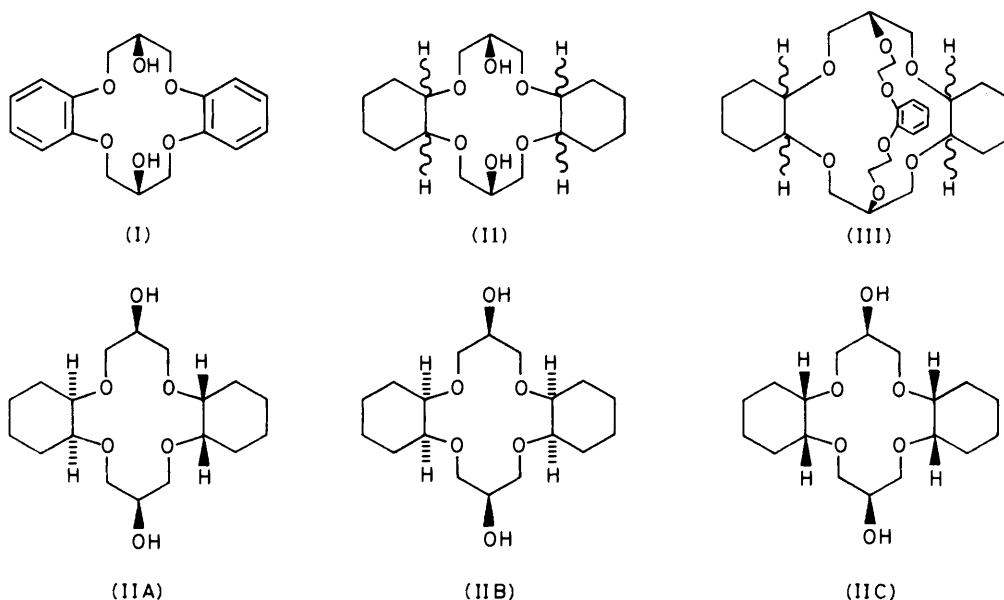
Table 2(b) indicates that the *X*-ray and neutron atomic co-ordinates are in reasonable agreement. The bond lengths are summarised in Table 3, which shows that, in all four analyses, the standard deviations obtained from least squares are about half those calculated from the spread about the mean values of chemically similar bonds. (The means of the C–C bonds in the cyclohexano rings do not differ significantly from those in the macrocyclic rings.) The value found by neutron diffraction for the carbon-carbon bonds is in good agreement with that, 1.537 Å, for cyclohexane itself.<sup>4</sup> There are no significant differences for C–C, C–O, and C–H distances from one isomer to another as determined by *X*-ray methods; (O–H distances are discussed below). Full tables of bond lengths and angles have been deposited as Supplementary Publication No. SUP 23760 (63 pp.).‡ The torsion angles are given in Table 4. There is no molecular symmetry to be found in isomer (A); isomers (B) and (C) are found to have (non-crystallographic) two-fold axes. [In solution, allowing for the boat-form of the cyclohexano rings, possible symmetries are *C*<sub>s</sub> for isomer (A) and *C*<sub>2v</sub> for isomers (B) and (C).] A comparison with the 14-crown-4 rings of the bicyclic molecules, (III), indicates that isomer (B) undergoes least change in conformation on forming the corresponding bicyclic molecule;<sup>2</sup> there is an interchange of *trans* and *gauche* about the C(3)–C(4) bond and about each of the O–C (cyclohexano) bonds. Both isomer (A)<sup>2</sup> and isomer (C)<sup>3</sup> undergo a further change, the C(6)–C(11) cyclohexano ring being inverted; the result is that while in all three diols O(1) and O(12) are axial, the equivalents of O(1) and O(5) are axial in the bicyclic molecules derived from isomers (A) and (C).

**Hydrogen Bonding.**—The geometry of the hydrogen bonding is displayed in Figure 3(a)–(c). There is a co-operative cyclic

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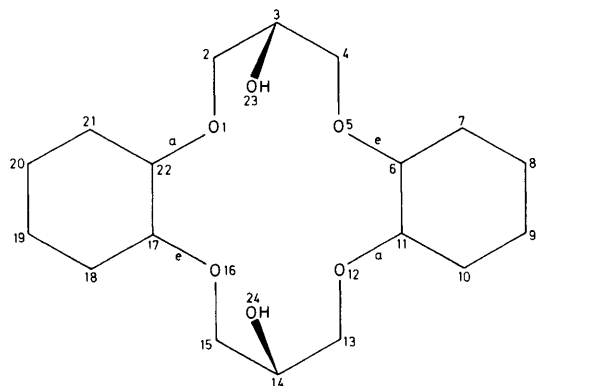
† The alternative numbering scheme, obtained by designating an oxygen atom as (1), as in the crystallographic numbering gives the names: (A), (*cis*-6,11,3,14-*trans*-17,22)-3,14-dihydroxy-1,5,12,16-tetraoxatricyclo[16.4.0<sup>6,11</sup>0<sup>17,22</sup>]docosane; (B), (*cis*-6,11,3,14,17,22)-3,14-dihydroxy-1,5,12,16-tetraoxatricyclo[16.4.0<sup>6,11</sup>0<sup>17,22</sup>]docosane; and (C), (*cis*-6,11,17,22-*trans*-3,14)-3,14-dihydroxy-1,5,12,16-tetraoxatricyclo[16.4.0<sup>6,11</sup>0<sup>17,22</sup>]docosane.

‡ For details of the Supplementary Publications Scheme see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1984, Issue 1.



**Table 1.** Crystal data for dicyclohexano-14-crown-4 diols,  $C_{18}O_2O_6$ ,  $M$  344.5

Isomer	(A)	(B) (X)	(B) (n)	(C)
M.p. ( $^{\circ}C$ )	137	118		170
$a/\text{\AA}$	12.010(3)	8.999(2)	9.005(5)	8.764(1)
$b/\text{\AA}$	12.700(2)	17.580(3)	17.588(7)	18.298(2)
$c/\text{\AA}$	13.290(3)	12.682(3)	12.715(11)	11.868(2)
$\beta/^{\circ}$	112.78(2)	108.71(2)	108.79(5)	
$V/\text{\AA}^3$	1 868.9	1 900.3	1 906.5	1 903.4
$D_m/g\text{ cm}^{-3}$	1.219	1.202		1.201
$Z$	4	4	4	4
$D_c/g\text{ cm}^{-3}$	1.216	1.204	1.200	1.202
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$Pn2_1a$
$\lambda/\text{\AA}$	0.709 26	0.709 26	1.237	0.709 26
$\mu(\lambda)/\text{mm}^{-1}$	0.083	0.083	0.295(3)	0.083
Crystal size (mm)	$0.33 \times 0.43 \times 0.48$	$0.95 \times 0.57 \times 0.38$	$2.75 \times 3.4 \times 5.0$	$0.12 \times 0.12 \times 0.30$
$2\theta_{\text{max}}$	50	56	80	50
$N_{\text{obs}}$	2 390	3 423	1 619	880
$R$	0.041	0.048	0.064	0.080
$wR$	0.052	0.047		0.072
Weighting scheme	$1/[\sigma^2(F_o) + 0.0017F_o^2]$	$1/\sigma^2(F_o)$	unit	$1/[\sigma^2(F_o) + 0.0039F_o^2]$
Shift (e.s.d.)	0.47	0.16		0.30
Difference electron density ( $e\text{ \AA}^{-3}$ )	0.34	0.23		0.25



**Figure 1.** Crystallographic numbering scheme for (II). Hydrogen atoms are numbered to correspond to the carbon or oxygen atoms to which they are attached. For  $CH_2$  groups the hydrogen atoms are distinguished further as  $H(n)a$  and  $H(n)b$ . For the OH groups  $H(23)a$  or  $H(23)b$  represent alternative positions for  $H(23)$ , similarly for  $H(24)$ .

system formed about a centre of symmetry for isomer (A), the bonds running 'right' or 'left' handed, according to the occupation of the 'a' or 'b' sites for the hydrogen atoms. The molecules are held in layers, parallel to the crystallographic (101) planes, by this hydrogen bonding. The crystal chemical unit of Table 2(a) takes part in one cyclic tetramer at  $\frac{1}{2}, 0, \frac{1}{2}$  through O(23) as illustrated in Figure 3(a) and in another at  $0, \frac{1}{2}, 0$  through O(24).

For isomer (B) the neutron results show no difference in the O-H bond lengths for the donor and non-donor hydrogen atoms; the latter has a larger vibration parameter. Of the oxygen atoms O(24), the donor, has a larger vibration parameter than the acceptor. The  $O \cdots O$  distances found by X-ray and by neutron diffraction are the same. The apparently shorter O-H bond obtained by X-rays is the result of well known physical effects.<sup>5</sup> It has been suggested<sup>6</sup> that it is valuable to 'correct' the OH distance by extension before discussing hydrogen bonding. For the X-ray values of isomer (B), and for isomer (C), we give in the legends to Figures 3(b) and (c) the results of this procedure.

In isomer (B) the hydrogen bonds are between molecules

**Table 2.** Atomic co-ordinates and vibration parameters for dicyclohexano-14-crown-4 diol isomers

In this Table

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i \cdot a_j)$$

The anisotropic vibration parameters have been deposited

(a) Isomer (A). Co-ordinates are  $\times 10^4$  for non-hydrogen and  $\times 10^3$  for hydrogen atoms.  $U_{eq}$  is ( $\times 10^4 \text{ \AA}^2$ )

Atom	x	y	z	$U_{iso}/U_{eq}^*$
O(1)	3 367(1)	3 137(1)	5 468(1)	489(6)*
C(2)	3 822(2)	2 225(2)	5 142(2)	484(8)*
C(3)	5 092(2)	2 452(1)	5 218(1)	412(7)*
C(4)	5 154(2)	3 273(2)	4 432(1)	485(8)*
O(5)	4 468(1)	2 937(1)	3 342.7(9)	443(5)*
C(6)	4 530(2)	3 630(1)	2 517(1)	419(7)*
C(7)	3 823(2)	3 121(2)	1 424(2)	467(8)*
C(8)	3 809(3)	3 803(2)	472(2)	610(10)*
C(9)	3 387(2)	4 914(2)	539(2)	549(9)*
C(10)	4 120(2)	5 401(2)	1 638(2)	528(9)*
C(11)	4 054(2)	4 736(1)	2 571(2)	428(7)*
O(12)	2 846(1)	4 612(1)	2 493(1)	433(5)*
C(13)	2 351(2)	5 512(2)	2 792(2)	473(8)*
C(14)	1 082(2)	5 242(2)	2 666(1)	473(8)*
C(15)	1 045(2)	4 354(2)	3 407(2)	476(8)*
O(16)	1 663(1)	4 728(1)	4 492(1)	545(6)*
C(17)	1 604(2)	4 080(2)	5 342(2)	492(8)*
C(18)	2 222(3)	4 689(2)	6 391(2)	552(9)*
C(19)	2 213(3)	4 087(2)	7 373(2)	682(11)*
C(20)	2 746(3)	2 998(2)	7 439(2)	627(10)*
C(21)	2 138(2)	2 393(2)	6 388(2)	588(10)*
C(22)	2 161(2)	3 001(2)	5 399(2)	485(8)*
O(23)	5 632(1)	1 489(1)	5 096(1)	509(6)*
O(24)	337(2)	4 985(1)	1 572(1)	567(6)*
H(2)a	328(2)	209(2)	433(2)	
H(2)b	387(2)	158(2)	568(2)	
H(3)	557(2)	273(2)	597(2)	
H(4)a	480(2)	395(2)	458(2)	
H(4)b	600(2)	335(2)	447(2)	
H(6)	538(2)	372(2)	259(2)	
H(7)a	299(2)	300(2)	136(2)	
H(7)b	412(2)	245(2)	134(2)	
H(8)a	458(2)	386(2)	47(2)	
H(8)b	327(2)	350(2)	-20(2)	
H(9)a	251(2)	495(2)	41(2)	
H(9)b	347(2)	532(2)	-2(2)	
H(10)a	384(2)	609(2)	168(2)	
H(10)b	497(2)	543(2)	178(2)	
H(11)	455(2)	506(2)	327(2)	
H(13)a	233(2)	613(2)	230(2)	
H(13)b	280(2)	570(2)	356(2)	
H(14)	73(2)	587(2)	287(2)	
H(15)a	19(2)	417(2)	327(2)	
H(15)b	144(2)	370(2)	328(2)	
H(17)	80(2)	391(2)	524(2)	
H(18)a	179(2)	535(2)	632(2)	
H(18)b	307(2)	483(2)	652(2)	
H(19)a	267(2)	450(2)	807(2)	
H(19)b	138(2)	401(2)	731(2)	
H(20)a	267(2)	264(2)	797(2)	
H(20)b	360(2)	308(2)	761(2)	
H(21)a	132(2)	226(2)	629(2)	
H(21)b	247(2)	173(2)	643(2)	
H(22)	168(2)	258(2)	474(2)	
H(23)a	520(4)	115(4)	444(4)	
H(23)b	570(4)	101(4)	575(4)	
H(24)a	74(4)	459(5)	133(4)	
H(24)b	16(5)	544(4)	118(4)	

**Table 2** (continued)(b) Isomer (B). Upper values are from X-ray diffraction; the co-ordinates for non-hydrogen atoms are ( $\times 10^5$ ), for hydrogen atoms ( $\times 10^4$ ),  $U_{eq}$  ( $\times 10^4 \text{ \AA}^2$ ). Lower values are for determination by neutron diffraction, the atomic co-ordinates are ( $\times 10^5$ ),  $U_{eq}$  and  $U_{iso}$  are ( $\times 10^3 \text{ \AA}^2$ ). The anisotropic vibration parameters for the non-hydrogen atoms have been deposited

Atom	x	y	z	$U_{eq}$
O(1)	-23 048(12)	73 433(6)	9 754(9)	445(4)
	-2 306(8)	7 346(3)	969(5)	48(2)
C(2)	-11 175(19)	71 512(10)	5 049(14)	458(6)
	-1 122(6)	7 156(3)	492(4)	44(2)
C(3)	4 223(19)	74 391(9)	12 867(14)	439(6)
	436(6)	7 443(3)	1 280(4)	43(2)
C(4)	9 010(19)	70 515(8)	24 073(14)	415(6)
	914(6)	7 046(2)	2 426(4)	42(2)
O(5)	10 491(12)	62 629(5)	22 427(8)	434(4)
	1 050(7)	6 275(3)	2 246(4)	43(2)
C(6)	18 992(17)	58 530(8)	32 208(12)	362(5)
	1 908(5)	5 863(2)	3 219(4)	35(2)
C(7)	11 844(20)	58 961(9)	41 509(13)	422(6)
	1 166(6)	5 895(3)	4 142(4)	45(2)
C(8)	21 756(22)	54 406(10)	51 543(13)	482(6)
	2 170(7)	5 444(3)	5 162(4)	52(2)
C(9)	23 648(24)	46 258(10)	48 382(14)	522(6)
	2 381(7)	4 616(3)	4 858(4)	52(2)
C(10)	29 989(20)	45 760(9)	38 696(14)	481(6)
	3 022(6)	4 573(3)	3 870(4)	47(2)
C(11)	20 228(17)	50 346(8)	28 728(13)	368(5)
	2 028(6)	5 030(3)	2 870(4)	37(2)
O(12)	5 067(12)	46 841(6)	24 552(8)	408(4)
	513(7)	4 681(3)	2 450(4)	43(2)
C(13)	-1 444(20)	47 088(10)	12 719(13)	464(6)
	-126(6)	4 708(3)	1 271(4)	49(2)
C(14)	-18 418(22)	44 634(9)	9 271(15)	539(6)
	-1 843(7)	4 461(3)	911(5)	54(2)
C(15)	-28 500(21)	49 884(9)	13 432(16)	522(6)
	-2 889(7)	4 990(3)	1 346(4)	53(2)
O(16)	-28 057(13)	57 265(6)	8 978(9)	485(4)
	-2 814(7)	5 724(3)	894(5)	48(2)
C(17)	-39 376(18)	62 492(9)	10 531(13)	426(5)
	-3 953(6)	6 240(3)	1 045(4)	44(2)
C(18)	-37 777(22)	63 880(11)	22 589(15)	519(6)
	-3 752(7)	6 384(3)	2 273(4)	54(2)
C(19)	-50 184(25)	69 538(12)	23 482(18)	617(8)
	-5 010(8)	6 950(3)	2 363(5)	64(2)
C(20)	-49 387(24)	76 891(11)	17 541(17)	579(7)
	-4 947(7)	7 700(3)	1 768(5)	61(2)
C(21)	-50 487(20)	75 466(10)	5 545(15)	511(6)
	-5 062(6)	7 549(3)	540(4)	52(2)
C(22)	-38 032(17)	69 875(9)	4 698(13)	414(5)
	-3 793(6)	6 986(3)	464(4)	43(2)
O(23)	3 889(15)	82 402(6)	14 613(11)	586(5)
	392(7)	8 234(3)	1 464(6)	56(3)
O(24)	-20 147(18)	37 059(7)	12 426(14)	776(6)
	-2 017(10)	3 708(4)	1 239(6)	78(3)
H(2)a	-1 096(20)	6 589(10)	422(14)	
	-1 029(14)	6 542(7)	412(10)	71(3)
H(2)b	-1 366(20)	7 387(10)	-238(15)	
	-1 366(15)	7 415(7)	-276(10)	76(3)
H(3)	1 185(20)	7 364(9)	853(14)	
	1 307(13)	7 350(6)	917(9)	65(3)
H(4)a	152(21)	7 148(9)	2 784(14)	
	30(14)	7 164(6)	2 796(9)	66(3)
H(4)b	1 898(22)	7 263(10)	2 890(14)	
	2 014(13)	7 287(6)	2 937(8)	67(3)
H(6)	3 005(21)	6 054(10)	3 501(14)	
	3 093(12)	6 082(5)	3 528(8)	58(2)
H(7)a	1 065(20)	6 412(10)	4 345(14)	
	1 104(14)	6 476(6)	4 402(9)	71(3)
H(7)b	108(22)	5 702(9)	3 871(15)	
	8(13)	5 684(6)	3 849(8)	63(3)
H(8)a	1 756(20)	5 481(9)	5 770(14)	
	1 634(14)	5 469(7)	5 811(10)	78(3)

Table 2 (continued)

Atom	x	y	z	$U_{eq}$
H(8)b	3 189(23)	5 694(9)	5 441(15)	
	3 317(14)	5 714(7)	5 471(9)	72(3)
H(9)a	2 997(21)	4 340(9)	5 456(15)	
	3 103(16)	4 326(7)	5 508(10)	85(3)
H(9)b	1 405(23)	4 379(10)	4 660(15)	
	1 228(15)	4 340(7)	4 632(10)	77(3)
H(10)a	4 074(22)	4 790(9)	4 062(14)	
	4 181(16)	4 806(7)	4 103(10)	84(3)
H(10)b	2 998(20)	4 033(10)	3 615(14)	
	3 094(16)	4 010(7)	3 623(10)	81(3)
H(11)	2 526(20)	5 033(10)	2 257(14)	
	2 578(13)	5 021(6)	2 234(9)	65(2)
H(13)a	-78(20)	5 233(10)	1 013(14)	
	-70(13)	5 278(6)	970(9)	64(3)
H(13)b	457(21)	4 357(9)	954(14)	
	504(14)	4 339(6)	921(9)	74(3)
H(14)	-2 176(20)	4 443(9)	109(15)	
	-2 261(14)	4 471(6)	24(9)	77(3)
H(15)a	-2 471(21)	5 016(10)	2 163(15)	
	-2 411(13)	4 996(6)	2 254(9)	70(3)
H(15)b	-3 943(22)	4 803(10)	1 120(14)	
	-4 033(15)	4 786(7)	1 072(10)	81(3)
H(17)	-4 956(22)	6 043(9)	677(14)	
	-5 101(14)	6 026(6)	642(9)	70(3)
H(18)a	-3 879(20)	5 901(10)	2 584(14)	
	-3 898(16)	5 851(8)	2 662(11)	90(3)
H(18)b	-2 738(22)	6 573(9)	2 641(15)	
	-2 644(14)	6 591(7)	2 669(10)	74(3)
H(19)a	-6 087(21)	6 705(10)	1 981(14)	
	-6 169(16)	6 689(7)	1 983(11)	90(3)
H(19)b	-4 876(20)	7 029(9)	3 113(15)	
	-4 907(17)	7 046(8)	3 190(11)	94(4)
H(20)a	-3 967(21)	7 965(10)	2 122(14)	
	-3 828(16)	7 965(7)	2 179(10)	79(3)
H(20)b	-5 758(21)	8 050(10)	1 793(14)	
	-5 868(15)	8 063(7)	1 800(10)	86(3)
H(21)a	-6 072(21)	7 337(9)	146(14)	
	-6 156(16)	7 308(8)	110(11)	82(3)
H(21)b	-4 884(19)	8 023(10)	197(14)	
	-4 922(14)	8 068(6)	150(9)	72(3)
H(22)	-3 922(19)	6 878(10)	-289(15)	
	-3 943(12)	6 868(6)	-402(8)	60(2)
H(23)	-424(23)	8 356(10)	1 569(16)	
	-652(17)	8 348(8)	1 513(12)	94(4)
H(24)	-1 680(22)	3 688(11)	1 920(16)	
	-1 457(15)	3 653(7)	2 032(10)	82(3)

(c) Isomer (C). Co-ordinates for the non-hydrogen atoms ( $\times 10^4$ ) and for the hydroxy hydrogen atoms ( $\times 10^3$ ) are given; those for the remaining hydrogen atoms have been deposited with the anisotropic vibration parameters.  $U_{eq}$  and  $U_{iso}$  are ( $\times 10^3 \text{ \AA}^2$ )

Atom	x	y	z	$U_{iso}/U_{eq}^*$
O(1)	1 532(8)	-1 411	-178(6)	55(2)*
C(2)	940(9)	-994(7)	-1 042(7)	39(2)*
C(3)	-467(9)	-618(7)	-703(7)	37(2)*
C(4)	-175(10)	-78(8)	227(8)	51(2)*
O(5)	894(7)	456(6)	-165(6)	56(2)*
C(6)	845(9)	1 136(7)	353(7)	42(2)*
C(7)	1 250(14)	1 138(7)	1 582(8)	81(2)*
C(8)	1 250(14)	1 916(7)	2 022(9)	95(2)*
C(9)	2 293(12)	2 429(8)	1 404(9)	74(2)*
C(10)	1 840(12)	2 421(6)	174(8)	51(2)*
C(11)	1 888(10)	1 643(7)	-247(8)	52(2)*
O(12)	3 430(7)	1 409(3)	-225(5)	40(1)*
C(13)	3 903(8)	981(7)	-1 211(6)	37(2)*
C(14)	5 372(9)	608(7)	-870(7)	37(2)*
C(15)	5 224(10)	44(7)	37(7)	43(2)*
O(16)	4 105(6)	-469(6)	-274(5)	42(2)*
C(17)	4 192(12)	-1 184(7)	266(7)	52(2)*
C(18)	3 885(12)	-1 142(7)	1 524(6)	63(2)*
C(19)	3 925(13)	-1 895(7)	2 052(11)	102(2)*

Table 2 (continued)

Atom	x	y	z	$U_{iso}/U_{eq}^*$
C(20)	2 907(13)	-2 420(7)	1 413(10)	83(2)*
C(21)	3 138(14)	-2 428(7)	160(9)	70(2)*
C(22)	3 080(10)	-1 671(6)	-355(7)	36(2)*
O(23)	-1 194(5)	-283(7)	-1 685(5)	54(2)*
O(24)	5 942(6)	305(6)	-1 845(6)	56(2)*
H(23)a	-60(4)	-21(4)	-225(4)	
H(23)b	-174(4)	-14(4)	-168(4)	
H(24)a	687(4)	8(4)	-176(4)	
H(24)b	517(4)	-1(4)	-202(4)	

related by screw axes so holding them in chains along the crystallographic *b* axis.

The isomer (C) molecules are held in double chains along the crystallographic *a* axis, the directions of the hydrogen bonds along each chain depending upon whether the 'a' or 'b' sites are occupied by the hydrogen atoms.

There is a good correlation with the i.r. spectra. In all three molecules the O...O distances are more than 2.7 Å, consistent with the appearance of hydroxy stretching bands at  $>3\ 000\text{ cm}^{-1}$ .

In isomer (B), as predicted from the sharp band at 3 560  $\text{cm}^{-1}$ , one hydrogen atom, designated H(23), is not acting as a donor. The band for the hydrogen bonded hydroxy group is 120  $\text{cm}^{-1}$  lower which compares with  $\Delta\nu$  of 141(2) and 134(7)  $\text{cm}^{-1}$  calculated (with the relationship of Bellamy and Owen<sup>7</sup>) from the hydrogen bonded O...O distances determined by X-ray and by neutron diffraction, respectively.

The individual hydrogen bonds in isomers (A) and (C), O-H...O or O...H-O, are disordered in the same way as those in ice,<sup>8</sup> although the co-operation is one-dimensional in (C), two-dimensional in (A), and three-dimensional in ice. The disorder, which may be static or dynamic, indicates that the crystal structures of these two isomers may be stabilized by entropic effects. It also gives the broadening of the hydroxy stretching frequencies so that individual values cannot be identified; the centres are at 230  $\text{cm}^{-1}$  for isomer (A) and 280  $\text{cm}^{-1}$  for isomer (C) from 3 560  $\text{cm}^{-1}$ , the position of the sharp band for isomer (B). Qualitatively these shifts correlate with the O...O distances 2.814(2) and 2.831(2) Å for isomer (A) and, the shortest, 2.776(10) and 2.738(9) Å for isomer (C). The  $\Delta\nu$  values calculated from these distances are 262(4) and 239(2)  $\text{cm}^{-1}$  for isomer (A) and 322(20) and 395(20)  $\text{cm}^{-1}$  for isomer (C), considerably greater than that observed.

**Packing of the Molecules.**—The melting points differ as might be expected if they depended inversely upon the strength of hydrogen bonding. A more subtle factor is the breaking of the weakest links, *i.e.*, the van der Waals interactions between layers in isomer (A) and around the columns of isomers (B) and (C).

Its greater density suggests that isomer (A) is more efficiently packed than isomers (B) and (C); this is unexpected because usually extensive hydrogen bonding reduces packing efficiency.

The neutron-diffraction study on isomer (B) provides reliable values for intermolecular contacts involving hydrogen atoms. Two symmetry-related hydrogen atoms are 2.38(2) Å apart, confirming the value of 1.2 Å suggested for the van der Waals radii.<sup>9</sup> There are also five shorter contacts, the minimum being 2.22(2) Å. As might be expected from the shorter C-H and O-H bond lengths, the values found by X-rays usually appear larger; the corresponding H-H distances are 2.54(3) and 2.30(3) Å.

We take H...H distances determined by X-rays of less than 2.5 Å as significantly short. Because the positions for the

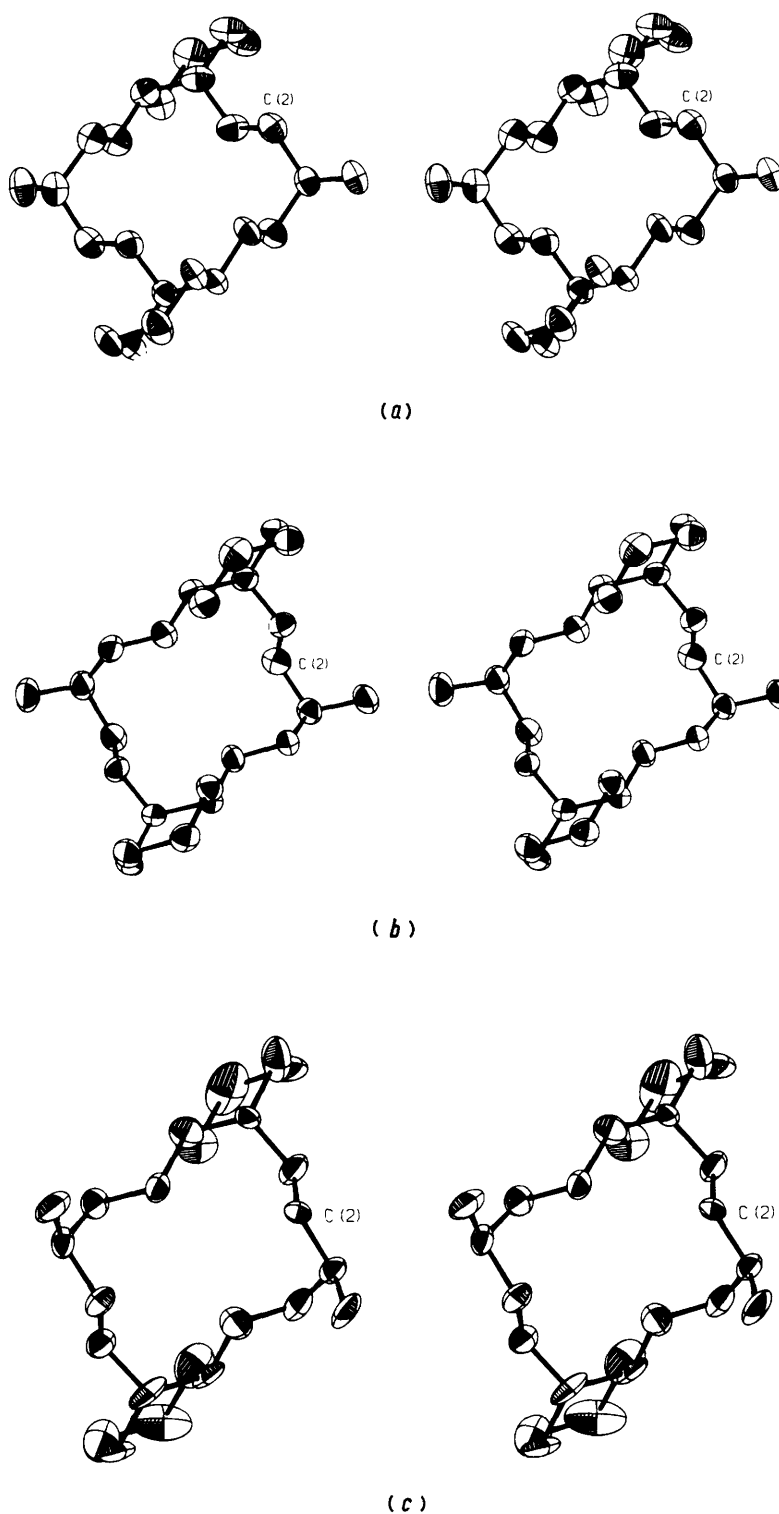


Figure 2. (a), (b), and (c), stereo views of isomers (A), (B), and (C), respectively

hydrogen atoms in isomer (C) were calculated to give the same average C–H bond length as found in isomer (B) by X-rays, and because both structures consist of hydrogen-bonded columns packed to give the same density, we compare the van der Waals contacts determined by X-ray diffraction. In both structures the packing gives contacts less than 2.5 Å from four hydrogen atoms in one molecule to hydrogen atoms in

other columns. Isomer (B) has no intermolecular C···H or O···H contacts less than 3.0 Å, while isomer (C) has one C···H and two O···H contacts less than 3.0 Å, *i.e.*, C(13)···H(3)<sup>v1</sup> 2.99 Å, O(1)···H(10)<sup>bv</sup> 2.72 Å, and O(12)···H(21)<sup>ix</sup> 2.73 Å. These correspond to the sums of the van der Waals radii with no evidence for C–H···O hydrogen bonding.<sup>9</sup> The packing of the columns appears more uniform,

**Table 3.** Summary of bond lengths (Å)

	Isomer (A)	Isomer (B)		Isomer (C)
		X-ray	Neutron	
C-C range	1.498—1.533	1.504—1.526	1.524—1.554	1.468—1.519
$\sigma$ (least squares)	0.003—0.004	0.002—0.003	0.006—0.008	0.008—0.014
C-C (mean)	1.516	1.515	1.537	1.503
$\sigma$ (individual)	0.009	0.006	0.009	0.016
$\sigma$ (mean)	0.002	0.002	0.002	0.005
C-O range	1.415—1.431	1.414—1.437	1.387—1.433	1.378—1.467
$\sigma$ (least squares)	0.002—0.003	0.002	0.006—0.009	0.010—0.013
C-O (mean)	1.423	1.426	1.421	1.424
$\sigma$ (individual)	0.005	0.008	0.014	0.035
$\sigma$ (mean)	0.002	0.002	0.004	0.011
C-H range	0.88—1.08	0.95—1.02	1.04—1.10	0.98(—)
$\sigma$ (least squares)	0.02—0.03	0.02	0.01	
C-H (mean)	0.98	0.98	1.07	
$\sigma$ (individual)	0.04	0.02	0.02	
$\sigma$ (mean)	0.007	0.004	0.004	

**Table 4.** Torsion angles in the 14-membered rings and in the cyclohexano rings. Estimated standard deviations are 0.2—0.3° for isomer (A), 0.1—0.2° for isomer (B) by X-ray, and 0.5—0.7° by neutron diffraction, and 0.7—1.1° for isomer (C)

	Isomer (A)	Isomer (B)		Isomer (C)
		X-ray	Neutron	
C(22)-O(1)-C(2)-C(3)	179	-168	-168	-167
C(17)-C(22)-O(1)-C(2)	-159	92	93	99
O(1)-C(2)-C(3)-C(4)	-66	64	64	64
O(1)-C(2)-C(3)-O(23)	169	-58	-58	-171
C(2)-C(3)-C(4)-O(5)	-60	60	60	60
O(23)-C(3)-C(4)-O(5)	64	-176	-176	-64
C(3)-C(4)-O(5)-C(6)	-176	164	163	155
C(4)-O(5)-C(6)-C(11)	-61	-177	-177	-173
C(11)-C(6)-C(7)-C(8)	55	59	60	54
O(5)-C(6)-C(11)-O(12)	-57	-64	-63	-61
C(10)-C(11)-C(6)-C(7)	-57	-58	-59	-59
C(6)-C(7)-C(8)-C(9)	-53	-56	-57	-57
C(7)-C(8)-C(9)-C(10)	53	54	53	57
C(8)-C(9)-C(10)-C(11)	-57	-54	-54	-56
C(9)-C(10)-C(11)-C(6)	59	55	56	60
C(6)-C(11)-O(12)-C(13)	165	96	96	94
C(11)-O(12)-C(13)-C(14)	-180	-170	-170	-164
O(12)-C(13)-C(14)-C(15)	62	63	62	67
O(12)-C(13)-C(14)-O(24)	-62	-62	-61	-171
C(13)-C(14)-C(15)-O(16)	63	61	61	54
O(24)-C(14)-C(15)-O(16)	-172	-173	-174	-66
C(14)-C(15)-O(16)-C(17)	172	169	169	158
C(15)-O(16)-C(17)-C(22)	62	-176	-177	-170
C(22)-C(17)-C(18)-C(19)	-56	58	60	58
O(16)-C(17)-C(22)-O(1)	54	-65	-65	-66
C(21)-C(22)-C(17)-C(18)	56	-58	-60	-59
C(17)-C(18)-C(19)-C(20)	54	-56	-57	-51
C(18)-C(19)-C(20)-C(21)	-54	55	55	51
C(19)-C(20)-C(21)-C(22)	55	-55	-55	-54
C(20)-C(21)-C(22)-C(17)	-55	56	58	56

but does not account for the higher melting point of isomer (C).

For isomer (A), between the layers there are no C...H or O...H contacts less than 3.0 Å, and four hydrogen atoms of one molecule make H...H contacts less than 2.5 Å with hydrogen atoms of molecules in other layers.

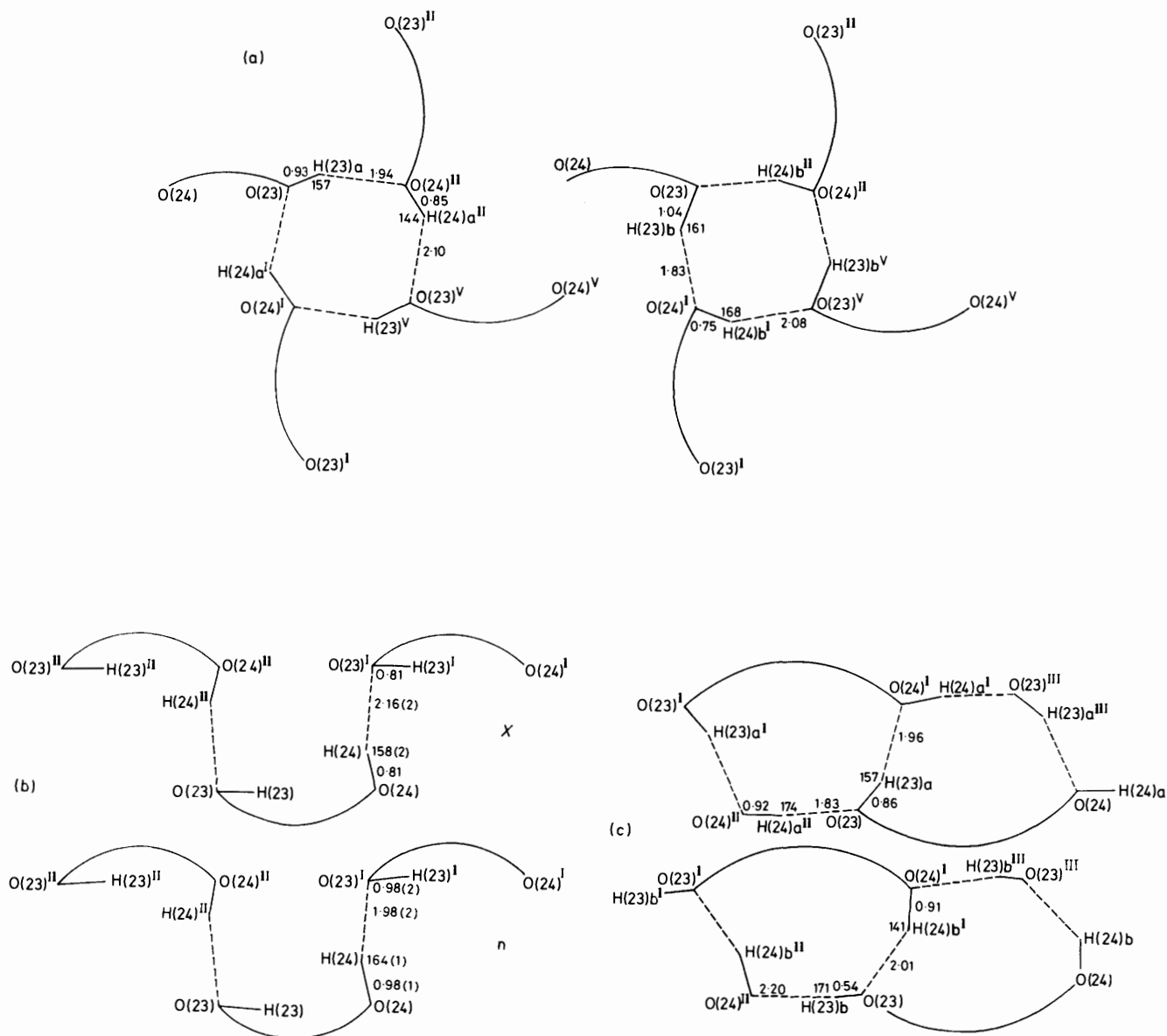
Full tables of intermolecular distances have been deposited in the Supplementary Publication.

### Experimental

**General Procedure.**—Melting points were determined using a Koffler hot-stage apparatus, i.r. spectra were recorded on a

Perkin-Elmer 457 spectrophotometer, and <sup>1</sup>H n.m.r. spectra recorded at 60 MHz on a JEOL PMX 60 spectrometer.

*cis*-9,20-Dihydroxy-7,11,19,21-tetraoxatricyclo[16.4.0.0<sup>12,17</sup>]-docosane. A suspension of the *cis*-dihydroxydibenzo-14-crown-4 (I) (22 g) in water (800 ml) containing the catalyst 5% Ru-Al<sub>2</sub>O<sub>3</sub> (1.5 g) was hydrogenated at 98 °C with good stirring at 100 atm pressure for 14 h. After filtering off the catalyst and washing with methanol, the product was concentrated to yield a pale yellow oil (22 g). This oil was dissolved in toluene (100 ml) and eluted through a neutral alumina column (25 × 1.5 cm) with toluene and concentrated to 250 ml and set aside at 3 °C. After 7 days substantially pure



**Figure 3.** (a) Hydrogen bonding in the crystal of isomer (A). The alternative arrangements about the centre of symmetry at  $1/2, 0, 1/2$  if the hydroxy hydrogen atoms occupy positions 'a' or 'b' are shown; in either case the  $O(23) \cdots O(24)^I$  distance is  $2.831(2)$  Å and the  $O(23) \cdots O(24)^{II}$  distance is  $2.814(2)$  Å. The standard deviation in the distances involving hydrogen atoms is  $0.05$  Å; the standard deviations in the angles at the hydrogen atoms range from  $4$  to  $6^\circ$ . Curves joining  $O(23)$  and  $O(24)$  represent molecules. The hydroxy group  $O(24)$  with  $H(24)a$  and  $H(24)b$  is hydrogen bonded to  $O(23)^{III}$  and  $O(23)^{IV}$ , respectively, in a cyclic system centred at  $0, 1/2, 0$ , the fourth oxygen atom being  $O(24)^V$ . The cyclic systems for  $O(23)^I$ ,  $O(24)^V$ , and  $O(23)^{II}$  are centred at  $1, 1/2, 1$ ;  $1, -1/2, 1$ ; and  $0, -1/2, 0$ , respectively. Roman numeral superscripts relate to the  $x, y, z$  co-ordinates of Table 2(a) by: I,  $1/2 + x, 1/2 - y, 1/2 + z$ ; II,  $1/2 - x, -1/2 + y, 1/2 - z$ ; III,  $-1/2 + x, 1/2 - y, -1/2 + z$ ; IV,  $1/2 - x, 1/2 + y, 1/2 - z$ ; V,  $1 - x, -y, 1 - z$ ; VI,  $-x, 1 - y, -z$ .

(b) The hydrogen bond in isomer (B) as determined by X-ray diffraction, X, and by neutron diffraction, n. The  $O(24) \cdots O(23)^I$  distances are  $2.925(2)$  and  $2.935(10)$  Å, respectively. Extension of the  $O(24)-H(24)$  bond to  $0.98$  Å in the X-ray structure gives  $H(24) \cdots O(23)^I$   $2.00$  Å with the angle at hydrogen  $157^\circ$ . Molecules are represented by curves joining  $O(23)$  and  $O(24)$ . The hydrogen bonds link the molecules in chains along the screw axes at  $0, y, 1/4$  and, with opposite polarity, at  $0, y, 3/4$ . Roman numeral superscripts refer to the equivalent positions: I,  $-x, -1/2 + y, 1/2 - z$ ; II,  $-x, 1/2 + y, 1/2 - z$ .

(c) Hydrogen bonding in the crystal of isomer (C). Alternative arrangements according to whether the hydroxy hydrogen atoms are in the 'a' site or the 'b' site are shown. The curves joining  $O(23)$  and  $O(24)$  represent the molecules. For molecules related by translation the  $O \cdots O$  distance is  $2.738(9)$  Å, e.g.,  $O(23) \cdots O(24)^{II}$  or  $O(24)^I \cdots O(23)^{III}$ ; for those related by a glide plane with translation  $a/2$  it is  $2.78(1)$  Å, e.g.,  $O(23) \cdots O(24)^I$  or  $O(24) \cdots O(23)^{III}$ . The double column shown is at  $x, 0, -1/4$  and the polarity of the O-H bonds is along the positive crystallographic  $a$  axis for sites 'a' and along the negative  $a$  axis for sites 'b'. The standard deviation in distances involving hydrogen atoms is  $0.04$  Å, in the angles at hydrogen it ranges from  $4$  to  $7^\circ$ . Extension of the O-H bonds to  $0.98$  Å gives negligible changes in the angles and reduces the  $H \cdots O$  acceptor distances for  $H(23)a, H(23)b, H(24)a, H(24)b$  to  $1.85, 1.76, 1.77,$  and  $1.95$  Å, respectively. Roman numeral superscripts correspond to the relations with respect to the  $x, y, z$  in Table 2(c): I,  $-1/2 + x, y, -1/2 - z$ ; II,  $-1 + x, y, z$ ; III,  $1/2 + x, y, -1/2 - z$ ; IV,  $1 + x, y, z$ .

isomer (C) was collected and recrystallised giving 2.1 g of colourless *needles*, (IIC), m.p. 170 °C, i.r. spectrum (Nujol) showed strongest bands at 3 280 (broad), 1 200, 1 150, 1 104 1 069, 964, 952, 895, 854, and 820 cm<sup>-1</sup> (Found: C, 62.8; H, 9.3%. C<sub>18</sub>H<sub>32</sub>O<sub>6</sub> requires C, 62.8; H, 9.3%). The filtrate from isomer (C) was concentrated to yield an oil which was dissolved in ether (100 ml). On standing, a second crop of very fine needles was obtained; these were collected and recrystallised from cyclohexane giving 1.9 g of pure *crystals*, isomer (A), (IIA), m.p. 134 °C, i.r. spectrum 3 330 (broad), 1 145, 1 132, 1 085, 1 054, 1 040, 980, 898, and 852 cm<sup>-1</sup> (Found: C, 62.89; H, 9.5%). The mother liquor was again concentrated to an oil and dissolved in ethyl acetate (60 ml) and rechromatographed through neutral alumina (30 × 2 cm); the product eluted with ethyl acetate (600 ml) was reconcentrated to an oil and dissolved in ether (100 ml). On standing, a mixture of isomers (A) and (C) separated, together with a small amount of isomer (B). Recrystallisation from cyclohexane (100 ml) gave a first crop of isomer (A) (0.6 g) followed by isomer (C) (0.5 g). The most soluble isomer (B) always crystallised from mixtures contaminated with varying amounts of isomers (A) and (C). However, isomer (B) normally separated in large prisms enabling a separation to be made by hand. These crystals were combined and recrystallised from cyclohexane, giving pure isomer (B), (IIB), colourless *prisms* (3.1 g), m.p. 118 °C, i.r. spectrum (Nujol) 3 560 (sharp), 3 440 (sharp), 1 205, 1 145, 1 110, 1 043, 1 015, 978, 956, 923, and 854 cm<sup>-1</sup> (Found: C, 63.2%; H, 9.3%). The total yields after repeated fractional crystallisation were isomer (A) 2.7 g, isomer (B) 3.2 g, and isomer (C) 2.9 g.

**X-Ray Crystal Structure Determinations.**—For X-ray diffraction, preliminary photographs were taken to establish space groups, and crystals were then mounted on an Enraf-Nonius CAD4 diffractometer and intensities collected by standard procedures. Two reference intensities were measured after every 50 normal reflections and no fall-off in intensity was noted. The unit cell dimensions and other relevant information are in Table 1.

The X-ray structures were solved by direct methods in SHELX;<sup>10</sup> and parameters refined by full matrix methods with anisotropic vibration for C and O atoms. In each structure the hydrogen atoms were located on difference maps and for isomers (A) and (B) their co-ordinates were refined. They were given a common isotropic temperature factor which was then refined. For isomer (B) the value was 0.0540(9) Å<sup>2</sup>. For isomer (A) there appeared to be two possible sites for each of the hydrogen atoms on the hydroxy groups and these were assumed to be of equal occupation, which was fixed at  $\frac{1}{2}$ ; these hydrogen atoms were given a common isotropic temperature factor which refined to 0.057(7) Å<sup>2</sup>, a value not significantly different from that, 0.060(1) Å<sup>2</sup>, for the hydrogen atoms on carbon. Refinement of the structure of isomer (C) in the space group *Pn2<sub>1</sub>a* gave molecular dimensions with pairs of bonds, one unreasonably long, the other short, indicating that the true structure might be centrosymmetrical, the 'average' molecule having a two-fold axis along *c*. To accommodate this, the space group had to be *Pnca*, *i.e.*, with a *c* glide perpendicular to *b*, and systematic absences of *h0l* with *l* odd. There are several reflections violating this absence. We attempted to ignore them and refine the structure. This gave an O...O' separation of 2.83 Å across a centre of symmetry with an unreasonable H(23)...H(23)' distance of 1.8(1) Å [reduced to 1.6(1) Å by extension of the O-H bond]. Even in *Pn2<sub>1</sub>a* there is a pseudo-centre of symmetry such that H(23) and H(24)' are still unreasonably close together. Further, in either space group there is another, and shorter, O...O contact. When an electron density difference map

was contoured, a low positive area was found in a position along this shorter O...O contact. Because of the pseudo-symmetry, however, this appeared at both ends so it was not possible to distinguish H(23) and H(24) (one along the 2.8 Å and one along the 2.7 Å contact) but on each oxygen the hydrogen atom can be at position 'a' or position 'b'. Along each column the 'a' sites or the 'b' sites may be occupied (Figure 3); the site occupation factor, constrained to 'a' + 'b' = 1, was treated as a parameter and the occupation was found to be 'a' 0.6, 'b' 0.4, consistent with 'a' giving the greater electron density. There were large correlation coefficients in the refinement in *Pn2<sub>1</sub>a* so a statistical test on the atomic positions was carried out. The results showed that, while the 14-crown-4 rings could be centrosymmetrically related, there were significant deviations for the carbon atoms of the cyclohexano rings and for the oxygen atoms. This is an example of parameter interaction<sup>11</sup> which limits the attainable reliability of the structure determination. In the final refinement, to give physically meaningful results the C(7)–C(8), C(8)–C(9), C(9)–C(10), C(18)–C(19), C(19)–C(20), and C(20)–C(21) bonds were constrained to have a common bond length. This target value refined to 1.512(3) Å.

In refinement the program SHELX<sup>10</sup> was used; scattering factors for C, O, and H were calculated from analytical coefficients taken from reference 12.

**Neutron Diffraction.**—The crystal of isomer (B) was mounted on the Australian Institute for Nuclear Science & Engineering's single crystal computer-controlled diffractometer at the 2tanA facility of the Australian Atomic Energy Commission's reactor HIFAR at Lucas Heights, New South Wales. Each observation required 5–10 min.; the reciprocal lattice to 2θ = 80° was explored at room temperature. Observations were corrected for absorption.

The co-ordinates obtained from the X-ray study were used as the starting point for refinement, which was carried out with SHELX on a CYBER 7600, at C.S.I.R.O., Canberra, ACT.

The scattering lengths used were *b<sub>c</sub>* 0.665, *b<sub>H</sub>* -0.372, *b<sub>O</sub>* 0.577 10<sup>-12</sup> cm. Anisotropic vibration was allowed for carbon and oxygen with individual isotropic vibration parameters for the hydrogen atoms.

Tables of observed and calculated structure factors, atomic vibration parameters, bond lengths and angles, and intermolecular distances have been deposited in the Supplementary Publication.

**Computing.**—All the molecular geometry was calculated with our suite of programs for the Prime 550; this computer was also used with ORTEP<sup>13</sup> to draw Figures 2(a)–(c) and with SHELX for the X-ray diffraction structure determination and refinement.

### Acknowledgements

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