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Self-recognition and hydrogen bonding by polycyclic bridgehead monoalcohols†

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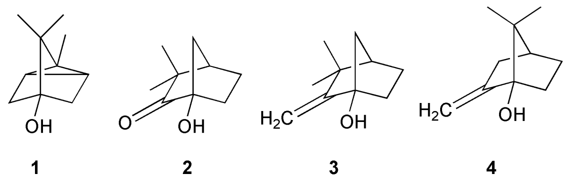
Our interest in the relationship between the hydrogen bonding motifs displayed by monoalcohols and the properties of the solids which contain these motifs has led us to determine the crystal structures of three polycyclic bridgehead monoalcohols. One $C_{10}H_{16}O$ isomer crystallises in the space group $P2_12_12_1$ but the three molecules which comprise the asymmetric unit are related approximately by the operations of a 3_1 screw axis. They are linked by hydrogen bonds to form an infinite helix. A second $C_{10}H_{16}O$ isomer forms rings containing four molecules joined by cooperative hydrogen bonds. The chiral space group $P4_12_12$ accommodates molecules of the *S,S* and *R,R* enantiomers in the molar ratio 92 : 8 (ee 84%) owing to disorder. A related $C_9H_{14}O_2$ keto-alcohol forms infinite chains by C–OH ··· O=C hydrogen bonding. These hydrogen bond motifs are shown to be typical for 45 tertiary monoalcohols, C_mH_nOH, present in the Cambridge Structural Database. Tertiary monoalcohols display in a more pronounced form the strong preferences for trigonal and tetragonal space groups and for asymmetric units containing several molecules which are established features of the crystallochemistry of monoalcohols.

Introduction

Intense interest is currently focused on crystal engineering techniques for the construction of porous organic frameworks from simple molecular building blocks. This interest is a natural consequence of the widespread view that crystals containing such frameworks have important potential applications as molecular sieves, dessicants, ion exchangers and catalysts.[1,2] Supramolecular interaction through hydrogen bonding has proved to be one of the more successful strategies for building such extended motifs.[3]

In this connection we have recently shown that crystals of the polycyclic cage alcohol 4-tricyclanol‡ **1** are held together by hydrogen bonds which link molecules related by a crystallographic 3_1 screw axis into helical chains. The packing of these chains generates nanometre-sized hydrophobic channels which run through the crystal parallel to the 3_1 axes. We believe that these structural features are associated with the markedly acicular habit adopted by crystals of **1**: the substance readily sublimes under normal laboratory conditions to give fine needles 2–3 cm long. This behaviour is unique among polycyclic cage alcohols.[4] Although the hydrophobic channels in **1** are too narrow (free diameter *ca.* 3 Å) for any of the potential practical applications, we considered it possible that species closely related to **1** (Scheme 1) might give rise to similar structures but with larger channels.



Scheme 1

To understand better how the shape of a polycyclic bridgehead alcohol molecule determines its preferred hydrogen bonding motifs in the solid, we have extended our structural studies from **1** to the tertiary alcohols **3** and **4**. Compounds **3** and **4** are isomeric with **1** but their carbon skeletons impose, respectively, less and more steric constraint on the ability of the hydroxy function to engage in hydrogen bonding. One tertiary and two secondary alcohols which are structural isomers of **1** have already been characterised crystallographically: adamantan-1-ol and adamantan-2-ol, respectively, form tetrameric[5] and hexameric[6] rings through hydrogen bonding; *cis*-verbenol§ is associated into infinite helical chains with *approximate* 3_1 symmetry but its crystals are prismatic rather than needle-shaped.[7]

We also report here the structure of **2** in which a ketonic oxygen atom capable of accepting hydrogen bonds replaces the terminal methylidene group of **3**.

The hydrogen bonding motifs displayed by monoalcohols were described briefly by Bernstein *et al.*[8] and more comprehensively in terms of graph set theory[9] by Brock and Duncan (hereafter BD).[10] The structural literature has grown substantially since 1994 when these surveys appeared. We therefore present a brief survey of hydrogen bonding in *tertiary* monoalcohols based on the current Cambridge Structural Database (CSD).[11]

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† Electronic supplementary information (ESI) available: crystallographic data for the structures **2**, **3** and **4** and bibliographic data for 45 structurally characterised monotertiary alcohols. See http://www.rsc.org/suppdata/ob/b2/b209427d/

‡ The IUPAC name for tricyclanol is 1,7,7-trimethyltricyclo[2.2.1.$0^{2,6}$]-heptan-4-ol.

§ The IUPAC name for verbenol is 4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-ol.

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Table 1 Hydrogen bonds in **2**, **3** and **4** [Å and °]

Compound	D–H ··· A	D–H	H ··· A	D ··· A	∠DHA	Operation *i*
2	O1–H1 ··· O2^i	0.82(3)	2.06(3)	2.778(1)	145(2)	$1 - x, y + ½, 1 - z$
3	O1–H1 ··· O2^i	0.84	1.93	2.749(3)	163	$x + 1, y, z$
3	O2–H2A ··· O3	0.84	1.90	2.736(3)	171	
3	O3–H3 ··· O1	0.84	1.90	2.723(3)	168	
4	O1–H1 ··· O2^i	0.74(2)	1.97(3)	2.708(2)	169(3)	$y + 1, x - 1, -z$
4	O2–H2 ··· O1	0.79(2)	1.96(2)	2.696(2)	154(2)	

Results

Description of the structure of 2

Molecules of the keto-alcohol **2** are linked into infinite chains by O–H ··· O hydrogen bonds (Table 1, Fig. 1) in which the OH group acts as a donor to the more basic carbonyl oxygen atom O2. The graph set defined by this motif is $C^1_1(5)$.[9] As expected,[12] the approach of the donor H atom to O2 [H ··· O2–C2 127°, H ··· O2–C2–C1 −4°] appears to be dictated by the direction of the O2 lone pairs. Successive molecules in each hydrogen-bonded chain are related by the operations of a crystallographic 2_1 screw axis which runs parallel to *b*. Viewed down the *b*-axis each chain is in contact with six similar chains. The efficient packing of these chains in **2** gives rise to a Kitaigorodski packing coefficient, C_K, of 0.694 which is typical for oxohydrocarbons.[13] The structure is free of voids or channels.

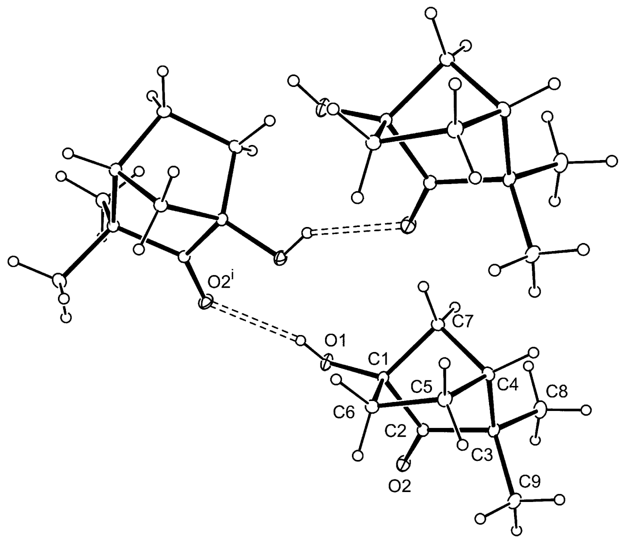


Fig. 1 A view of the hydrogen bonded chain in **2**. The molecules shown are linked by operations of the 2_1 screw axis parallel to *b* and the atom numbering is indicated. Here and in Figs. 2 and 3 20% probability ellipsoids are shown.

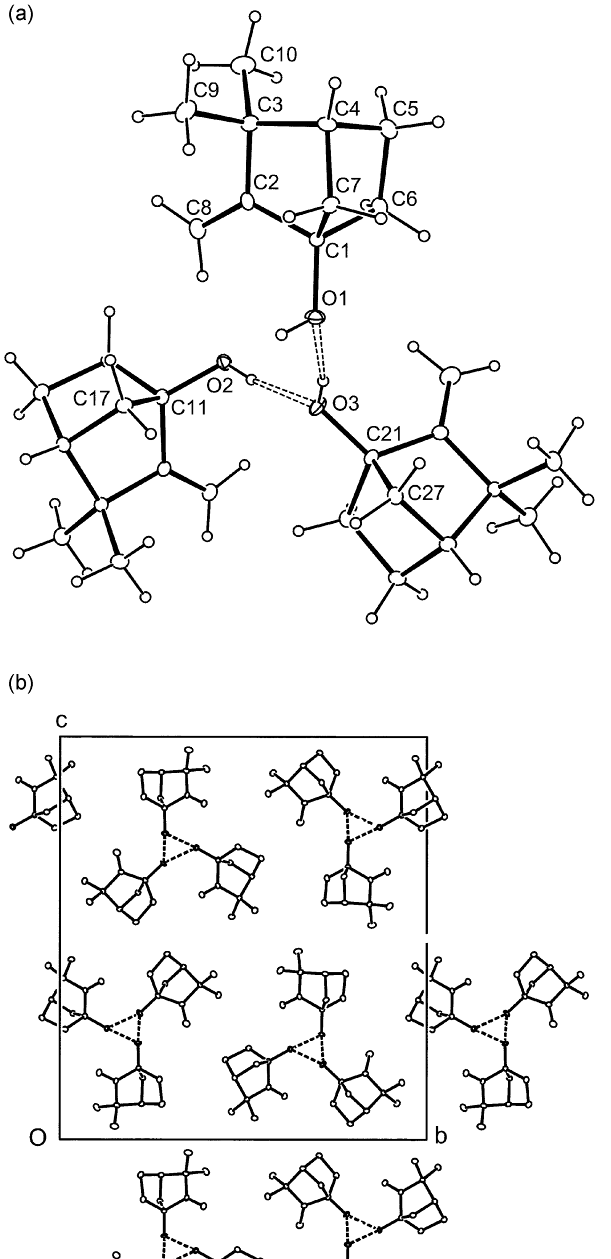


Fig. 2 (a) The asymmetric unit of **3** viewed down the *a*-axis. The three crystallographically independent molecules (**3a**, **3b**, **3c**) are related by a *pseudo*-3_1 axis parallel with the *a*-axis. Atom numbers are shown for molecule **3a**; corresponding carbon atoms in **3b** and **3c** are numbered C1*n* and C2*n*. Not shown is the hydrogen bond from O1 to O2^i (*i*: $x-1, y, z$). (b) The crystal packing viewed down the *a*-axis. Hydrogen atoms are omitted for clarity.

Description of the structure of 3

Replacement of the keto group of **2** by the methylidene group of **3** leads to a completely different molecular arrangement in the solid state. The asymmetric unit (Fig. 2a) comprises three molecules of the *R,R*-alcohol (**3a**, **3b** and **3c** containing respectively atoms O1, O2 and O3). These molecules are structurally almost indistinguishable and they are linked by O–H ··· O hydrogen bonds into a helical chain which runs parallel to the *a*-axis (Table 1). The sequence O2 ⟶ O3 ⟶ O1 ⟶ O2^i (*i*: $x + 1, y, z$) involves successive rotations about the *a*-axis by 105, 134 and 121° followed in each case by a translation of *ca.* *a*/3 (Fig. 2). Detailed inspection of the translations and rotations which map each molecule onto the next in the chain and of the coordination of each oxygen atom (Table 2) confirms that the chains of hydrogen-bonded molecules deviate only slightly from 3_1 symmetry. Viewed down the *a*-axis each chain is found to be surrounded by six others (Fig. 2b). Although the packing is slightly less efficient than in **1** since $C_K = 0.656$ (*cf.* **1** $C_K = 0.663$), there are no voids or channels in the structure. The structure is strongly reminiscent of that of *cis*-verbenol[7] in that

Table 2 Selected angles (°) in the hydrogen bond networks of **3** and **4**[a]

O atom	$C_\alpha OO_\alpha$	$C_\alpha OO_\beta$	$O_\alpha OO_\beta$	$C_\beta C_\alpha OO_\alpha$	$C_\beta C_\alpha OO_\beta$
3 O1	102.7	134.3	113.9	49.0	−167.7
3 O2	113.4	137.2	98.7	48.7	−176.2
3 O3	117.1	133.4	109.1	37.2	−152.0
4 O1	113.1	144.8	83.7	−126.6	−13.3
4 O2	128.3	134.1	93.0	35.8	−113.2

[a] C_β is the bridgehead carbon atom: C7, C17 or C27 in the three independent molecules of **3** and C7 or C17 in **4**.

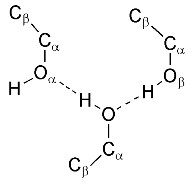


Table 3 Bond length ranges (Å) in tertiary alcohols **2**–**4**[a]

Bond	**2** (X = O)	**3** (X = CH_2)	**4** (X = CH_2)
C–OH	1.400(2)	1.415(3)–1.424(3)	1.411(2)
C–C	1.514(2)–1.550(2)	1.514(4)–1.561(5)	1.520(2)–1.553(2)
C=X	1.210(2)	1.315(5)–1.318(4)	1.328(2)

[a] Values for the disordered molecule in **4** are subject to systematic error and have been disregarded in compiling this table.

both it and **3** crystallise in $P2_12_12_1$ with three independent molecules defining a pseudo-3_1 axis. The cell edge parallel with this axis is appreciably longer in *cis*-verbenol (7.01 Å) than it is in **3** (5.97 Å). The crystals are fine needles elongated along the direction of the pseudo-3_1 screw axis.

Description of the structure of 4

The packing of **4** is based on a group of four alcohol molecules arranged around a crystallographic diad axis and linked into a ring by hydrogen bonding (Fig. 3a). The resulting $R^4_4(8)$ graph set defines the most common hydrogen bonding motif displayed by monotertiary alcohols and indeed by mono-alcohols in general (see below). This motif requires that the O ··· O ··· O angles defined by hydrogen-bonded oxygen atoms should be more acute than the corresponding angles in chain structures like **3** (Table 2). The packing coefficient, C_K, is 0.665, virtually the same as in **1** and **3**.

An interesting feature of the structure of **4** is that the crystal used for X-ray analysis is not optically pure, although the space group ($P4_12_12$) involves only rotational symmetry operations. The asymmetric unit contains two nearly identical molecules of the *S,S* isomer. However, during refinement it became clear that the site occupied by molecule 1 contained 0.833(3) of the *S,S*-isomer and 0.167(3) of the *R,R*-isomer. Only the sites of O1, C5, C6 and C10 appear to be common to both isomers (Figs. 3b and 3c). Molecule 2 does not appear to participate in the disorder. The enantiomeric excess in the crystal used for the X-ray analysis is 84% – almost the same as that of the (−)-(1*R*)-fenchone¶ sample used in the synthesis of **4** (see below). Crystals of **4** do not contain solvent-accessible voids. Indeed, if the disorder is ignored, the packing coefficient, C_K, is 0.656 – virtually identical to that for **1**.

Bond lengths (Table 3) and angles in **2**, **3** and the ordered molecule of **4** are unexceptional. The C–OH distances in **3** and **4** [1.411(2)–1.419(3) Å] are slightly longer than that in **2** [1.400(2) Å] where the alcohol oxygen atom does not act as a hydrogen bond acceptor. The disordered molecules in **4** show some untypical bond distances which indicate that the atomic positions are subject to systematic error.

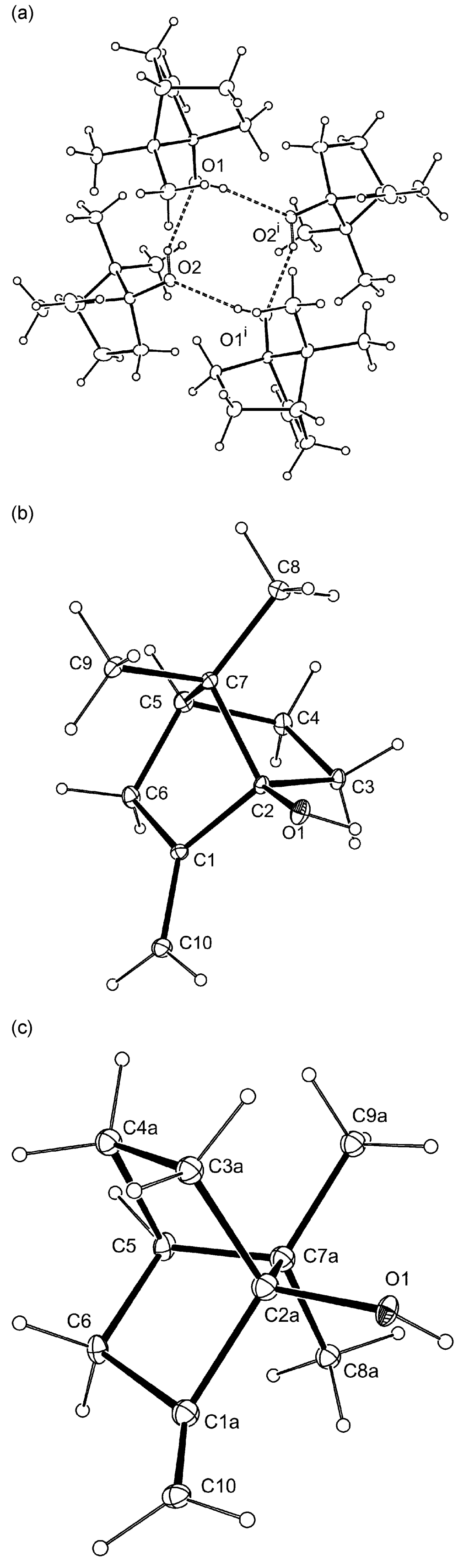


Fig. 3 (a) The $R^4_4(8)$ tetrameric ring formed by the two independent molecules of **4** and their diad-related symmetry equivalents. (b) The *S,S* component [occupancy 0.833(3)] of the disordered site in **4**. (c) The *R,R* component of the disordered site. Only C5, C6, C10 and O1 are common to both components.

¶ The IUPAC name for fenchone is 1,3,3-trimethylbicyclo[2.2.1]heptan-2-one.

Table 4 Distribution (%) of structures by (a) crystal system and (b) number of molecules per asymmetric unit, Z', for (A) all 245392 structures in the CSD, (B) 252 monoalcohols C_mH_nOH, (C) 45 monotertiary alcohols containing a $C(sp^3)$–C–OH fragment and (D) 55 monoalcohols discussed in ref. 10

(a) Crystal system: a – triclinic, m – monoclinic, o – orthorhombic, t – tetragonal, r – trigonal, h – hexagonal, c – cubic.

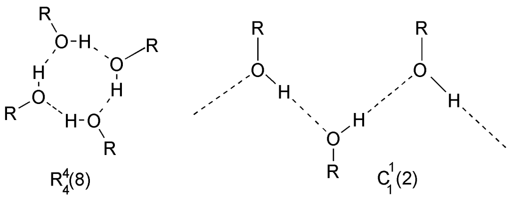
Group	a	m	o	t	r	h	c
A	22	53	20	2.3	1.6	0.5	0.4
B	18	51	13	9.1	8.3	–	–
C	27	33	11	16	13	–	–
D	16	47	15	16	5.5	–	–

(b) Number of molecules per asymmetric unit, Z'.

Sample	$Z' > 1$	$Z' = 2$	$Z' = 3$	$Z' = 4$
A	8.3	7.3	0.4	0.3
B	42	27	8	4
C	60	40	11	9
D	42	29	11	1.8

Discussion

In their survey of monoalcohols, ROH where R = C_mH_n, BD noted that the proportion of structures in trigonal or tetragonal space groups is about five times greater than it is in the database as a whole. Likewise, structures with asymmetric units containing more than one molecule ($Z' > 1$) are also about five times more common than would be expected. They rationalised these findings in terms of the formation of $C_1^1(2)$ chains (Scheme 2) in which the relative positions of the R groups are constrained by the geometry of the O–H ··· O hydrogen bonds: the bulk of adjacent R groups precludes them from being related by simple lattice translations or by 2_1 screw axes, hence the preference for 3_1 helices. $R_4^4(8)$ Ring tetramers also allow sufficient space for the R groups and easily arrange themselves in tetragonal space groups.[10] Since these findings are consistent with the structures of **1**, **3** and **4** we have thought it worthwhile to see how applicable they are to the whole group of tertiary alcohols which have now been structurally characterised. Accordingly, we present in Table 4 statistics on the frequency of occurrence of each crystal system and of various values of Z' for (A) all structures in the current CSD; (b) 252 homomolecular structures containing monoalcohols, ROH where R = C_mH_n (this group is comparable to that studied by BD but is nearly five times as large); (C) the subset of (B) composed of 45 monotertiary alcohols containing a $C(sp^3)$–C–OH fragment and thus comparable to **1**, **3** and **4**; (d) the 55 structures originally analysed by BD.[10,11] Tetragonal and trigonal structures together account for 29% of the tertiary alcohols in (C), compared with 17 and 22% of samples (B) and (D) and for only 3.9% of all structures in the database. Similarly, 60% of structures in (C) have $Z' > 1$; this compares with 42% for samples (B) and (D) and 8.3% for all structures. This is consistent with the arguments of Brock and Duncan, since among all ROH molecules tertiary alcohols *as a class* are likely to have the most sterically demanding R groups.



Scheme 2

A detailed analysis of the hydrogen bonding motifs in the 45 structures of group C is presented in Table 5. For 11 of these tertiary alcohols the motif is finite (graph set symbol D) and the full hydrogen bonding ability of the OH group as donor and acceptor is not used. The most common arrangement, found in nearly half of the structures, is the $R_4^4(8)$ tetrameric ring (Scheme 2), variously displaying $\bar{4}$, 2, $\bar{1}$ or no symmetry at all (other than the identity operation). One $R_6^6(12)$ hexamer and three $R_3^3(6)$ trimers also occur. The $R_6^6(12)$ motif is ubiquitous in the various polymorphs of ice[14] and its rarity among alcohols is a little surprising. Steric reasons do not seem to preclude the $R_5^5(10)$ motif for an isolated structure; its incompatibility with the symmetry allowed in Bravais nets probably explains its absence from Table 5. Of the eight $C_1^1(2)$ chain structures six resemble **1** and **3** in that they have either exact or approximate 3_1 symmetry.[15] The lattice translation parallel to the three-fold screw axis shows some variation in length (6.0–7.3 Å) for the six structures already in the CSD, while the corresponding axis of 5.97 Å for **3**, which belongs to this structural group, lies at the lower end of this range.

Table 5 Number (n) of monotertiary alcohols of group C adopting different hydrogen bond motifs. Each motif is specified by its graph set symbol.[9] The structures in each graph set are subdivided according to the different combinations Z' and S. Z' is the number of independent molecules and S the Hermann–Mauguin symbol for the symmetry operations (other than lattice translations) needed to complete the motif

	$C_1^1(2)$		$R_3^3(6)$		$R_4^4(8)$		$R_6^6(12)$		D
	Z', S	n	Z', S	n	Z', S	n	Z', S	n	n
	2, 1	2	1, 3	1	1, $\bar{4}$	6	1, $\bar{3}$	1	11
	1, 3_1	4	3, 1	2	2, $\bar{1}$	7			
	3, 1	2[a]			2, 2	5			
					4, 1	4			
Totals		8		3		22		1	11

[a] Both show approximate 3_1 pseudo-symmetry.

Finally, we have checked the structures based on the 3_1 chain arrangement and also the apparently open $R_6^6(12)$ motif with the VOID option in PLATON:[16] none contains channels even as narrow as those found in **1**.

Experimental

Samples of **2**, **3** and **4** were prepared by established methods.‖ Thus, keto-alcohol **2** was prepared from (+)-(1*R*)-camphor by the method of Nickon *et al.*[17] It should be noted that these authors describe a synthesis from (+)-(1*R*)-camphor but show the alternative, incorrect enantiomers in their diagrams. Alcohol **3**, see also Libman *et al.*,[18] and alcohol **4** were respectively prepared from (+)-(1*R*)-camphor and (−)-(1*R*)-fenchone by the method of Martínez *et al.*[19] Our sample of (−)-(1*R*)-fenchone, obtained from Aldrich, showed $[a]_D = -57.0\ 10^{-1}$ deg cm^2 g^{-1} recorded at 20 °C in ethanol, identical to that for which chiral HPLC gave an ee of 82%.[20] The synthetic steps which generate **4** from (−)-(1*R*)-fenchone are most unlikely to cause further racemisation.

Single crystals for X-ray analysis were obtained by sublimation of the relevant compound placed in a conical flask with a ground glass stopper. The sublimations were effected at ambient temperatures in diffuse daylight.

All crystallographic measurements (Table 6) were made on a Nonius KappaCCD diffractometer with Mo–Kα radiation, $\lambda = 0.70173$ Å, at 100 K. Absorption corrections were not deemed necessary. All independent reflections were used in the least-squares refinements, which were on F^2 with weights chosen to give a goodness-of-fit near unity. Absolute configurations are based on the chemical provenance of each sample and were not determined experimentally. In **4** the site of

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‖ CCDC reference number(s) 195489–195491. See http://www.rsc.org/suppdata/ob/b2/b209427d/ for crystallographic files in .cif or other electronic format.

Table 6 Crystal data and structure refinements.

Compound	**2**	**3**	**4**
Empirical formula	$C_9H_{14}O_2$	$C_{10}H_{16}O$	$C_{10}H_{16}O$
Formula weight	154.20	152.23	152.23
Crystal system	Monoclinic	Orthorhombic	Tetragonal
Space group	$P2_1$	$P2_12_12_1$	$P4_1 2_1 2$
a (Å)	6.1182(3)	5.9714(1)	10.7633(1)
b (Å)	6.6921(4)	20.5466(5)	
c (Å)	10.1810(5)	22.5632(6)	31.3398(5)
β(°)	94.019(3)		
U (Å^3)	415.82(4)	2768.32(11)	3630.67(8)
Z	2	12	16
Dcalc/Mg m^{-3}	1.232	1.096	1.114
μ/mm^{-1}	0.085	0.068	0.069
F(000)	168	1008	1344
Crystal size/mm	0.25 × 0.18 × 0.08	0.75 × 0.06 × 0.04	0.38 × 0.33 × 0.15
θ max (°)	30.0	25.1	33.1
Index ranges	$\|h\|\leq 8, \|k\|\leq 9, \|l\|\leq 14$	$\|h\|\leq 7,\|k\|\leq 23,\|l\|\leq 27$	$\|h\|\leq 16, \|k\|\leq 11,\|l\|\leq 44$
No. measured	4157	15934	22563
No. unique [R_{int}]	2340 [0.036]	2845 [0.069]	4009 [0.032]
No. of Friedel pairs	1024	—	—
Data/parameters	2340/108	2845/304	4009/234
$R1$, $wR2$ (all data)	0.054, 0.093	0.067, 0.108	0.061, 0.132
$\|\Delta\rho\|$ (e Å^{-3})	0.26	0.21	0.24

molecule 1 contains a disordered mixture of enantiomers and the atomic positions are therefore subject to some systematic error. Friedel pair intensities were averaged prior to final refinement for **3** and **4**. Hydroxy H atoms were freely refined for **2** and **4** but a riding model was considered more appropriate for **3**.[21]

Acknowledgements

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