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# DIALCOHOL HYDROGEN BONDED LADDER STRUCTURES

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*Appropriate dialcohols have the ability to form unidirectional ladder structures on crystallisation from solution. These assemblies are built from two internally hydrogen bonded molecular strands which are cross-linked by further hydroxy group hydrogen bonding. In staircase-ladder structures the molecules of the two strands are out of phase and linked by $(O\text{-}H)_n$ chains. Alternatively, if the molecules of the two strands are in phase, a step-ladder structure results where the dialcohol units are linked by $(O\text{-}H)_4$ cycles. Both ladder types show strong enantiomer ordering and symmetry preferences. For example staircase-ladders normally comprise dialcohol molecules of one handedness surrounding a $2_1$ screw axis. New racemic dialcohols are described which form staircase-ladders. Self-resolution, guest inclusion, enantiomer ordering, and asymmetric unit phenomena are described which result in previously unobserved types of staircase-ladder assembly.*

*Keywords*: hydrogen bonding; hydroxy groups; enantiomer packing; molecular ladders; inclusion compounds; supramolecular synthons

## INTRODUCTION

Certain dialcohol molecules crystallise from solution as unidirectional staircase-ladder or step-ladder assemblies [1]. These are double-stranded structures with hydroxy group hydrogen bonding both within, and between, the two strands of molecules (Fig. 1). The parallel strands of dialcohols may be compared to the uprights of a household ladder, and the inter-strand hydrogen bonding to its rungs. The staircase- and step-ladders differ respectively through the dialcohol molecules of their strands being out of phase and linked by $(O\text{-}H)_n$ zigzag chains, or in phase and linked by $(O\text{-}H)_4$ cycles, of hydrogen bonds.

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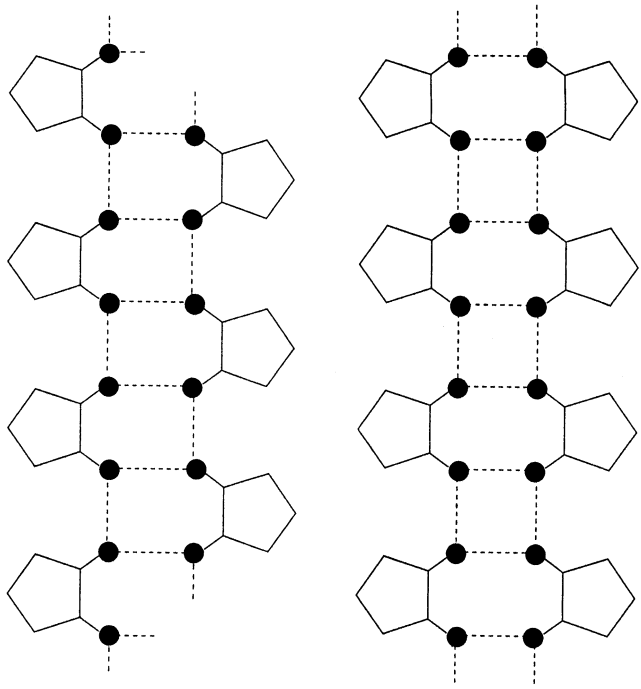

**FIGURE 1** Diagrammatic representation of (left) staircase-ladder and (right) step-ladder assemblies. The five-membered cycles represent schematic dialcohol molecules, the filled circles their hydroxy groups, and the dashed lines the $\cdots$O-H$\cdots$O-H$\cdots$O-H$\cdots$ hydrogen bonding motifs.

## RESULTS AND DISCUSSION

A search for X-ray structures of dialcohol ladders was performed using the Cambridge Structural Database (CSD) [2] making no assumptions regarding chirality or symmetry. The survey was deliberately limited to compounds containing C, H and two hydroxy groups only. It located twenty eight examples, made up of sixteen staircase-ladder and twelve step-ladder structures. The molecular structures vary considerably and the alcohol groups may be primary, secondary, or tertiary [1]. The range of O$\cdots$O separation distances within the dialcohol molecules was 3.47–5.39 Å for the staircase-ladders, but 2.72–6.43 Å for the step-ladders. The greater tolerances in the latter case are understandable since the partners from opposite strands are simply positioned opposite each other. In contrast, the O$\cdots$O distance in the former case has to be compatible with construction of the hydrogen-bonded chain motif (see Fig. 1).

There are very definite structural and symmetry preferences observed within both classes. All sixteen staircase-ladders had $2_1$ screw axis symmetry. No other types of staircase-ladder construction were recorded. In one case the dialcohol building block was achiral, but in the other fifteen the molecules within each ladder were enantiomerically pure. Of these, nine compounds were already resolved at the outset but six were racemic substances. Two of the racemic dialcohols underwent spontaneous self-resolution [3,4] to give a conglomerate: in other words a mixture of crystals was produced containing only pure (−)- or pure (+)-ladders [5,6]. The remaining four racemic compounds yielded crystals containing a 1:1 mixture of (−)- and (+)-ladders.

Ten of the twelve dialcohols forming step-ladders were racemic, two were achiral, and none were enantiomerically pure substances either before or after crystallisation. Of these ten handed compounds, nine crystallised with ladders containing both enantiomers and eight gave structures with enantiomerically pure strands. The preferred ladder construction (6 cases out of the 12) had centres of symmetry located both in the middle of the $(O\text{-}H)_4$ cycles and between the molecules of each strand.

Dialcohols **1** [7] and **2** [8] (Fig. 2) are examples which illustrate these two favoured ladder construction modes. Their double-stranded hydrogen bonded ladders are illustrated in Figure 3.

To investigate ladder-forming behaviour we have synthesised a number of new dialcohol molecules which we felt might also assemble in this manner [1]. Among these is the alicyclic compound **3** discussed here. For

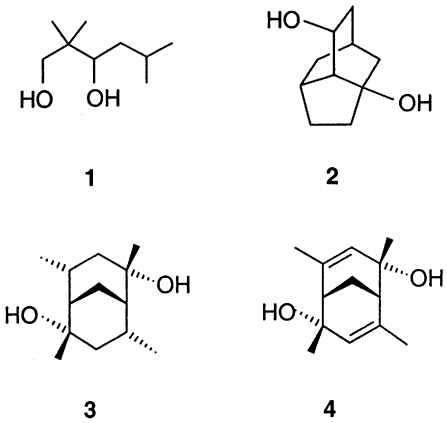


**FIGURE 2** Molecular structures of the dialcohols **1**–**4** discussed in this paper. All four have solid state structures which contain double-stranded hydrogen-bonded ladders.

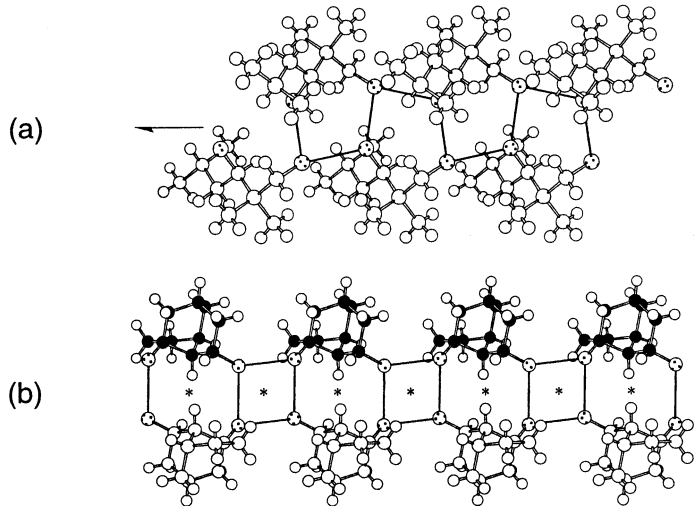


**FIGURE 3** Examples of the preferred double-stranded staircase- and step-ladder structures formed by dialcohols. Oxygen atoms are stippled and hydrogen bonds are indicated by solid lines. (a) The staircase-ladder formed by **1** molecules of the same handedness arranged around a $2_1$ screw axis. (b) The step-ladder formed by **2** where each strand is enantiomerically pure but of opposite handedness to the other (indicated by black and white carbon atoms). The star symbols represent centres of symmetry.



some time we have been working on the design and synthesis of new dialcohol inclusion compounds [9–12]. We were therefore pleased to discover that **3** not only forms molecular ladders but can also be an excellent new lattice inclusion host [13,14]. Despite our experience in the field this latter property was totally unexpected.

Crystallisation of racemic **3** from tetrahydrofuran resulted in spontaneous self-resolution and formation of a conglomerate. No guest inclusion was observed from this solvent. The X-ray determination revealed packing in the chiral space group $P2_12_12_1$ and a hydrogen bonded staircase-ladder structure where molecules of the same chirality are arranged around a $2_1$ screw axis (Fig. 4a). From our CSD survey we recognise that this behaviour is entirely typical for a dialcohol which undergoes self-assembly to produce a staircase-ladder.

In contrast, when racemic **3** was crystallised from several other solvents a series of inclusion compounds $(\mathbf{3})_2$·(guest) were produced. These were isostructural in space group $P2_1/c$ and contained both dialcohol enantiomers. X-ray investigation revealed that these compounds were also built from staircase-ladders, but of a new and different type [15]. One strand was

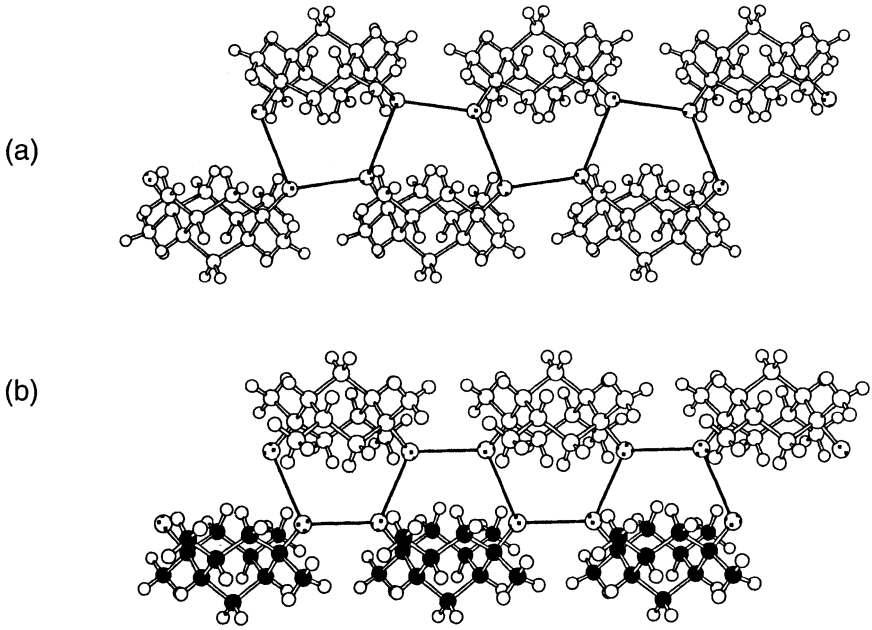


**FIGURE 4** (a) The resolved staircase-ladder structure formed by **3** on crystallisation from tetrahydrofuran. Dialcohol molecules of the same handedness surround a $2_1$ screw axis. (b) The different staircase-ladder present in $(\mathbf{3})_2$·(chlorobenzene) where the two hydrogen bonded strands are chirally pure but of opposite handedness (carbons coloured black or white).



built from (+)- and the other from (−)-dialcohol molecules. Figure 4b illustrates this ladder construction for the example of $(\mathbf{3})_2$·(chlorobenzene). The ladders pack parallel to each other along *a* with the guest molecules occupying interstitial sites between them. Only dispersion forces operate between hosts and guests.

The racemic dialcohol **4** was found not to undergo self-resolution or to trap guests. Crystals grown from chloroform, however, involve staircase-ladders of yet another type which are illustrated in Figure 5. The enantiomer ordering is related to that observed in $(\mathbf{3})_2$·(guest) except that there is an additional complication. Two independent molecules (A and B) are present in the unit cell of this structure. Consequently there are equal numbers of A-(+)/B-(−) and A-(−)/B-(+) ladders present in each crystal of **4**. Alcohols are capable of participating in many hydrogen bonding motifs [16]. Pure simple dialcohols prefer to hydrogen bond with one donor and one acceptor per hydroxy group, and frequently adopt linear chain, helical

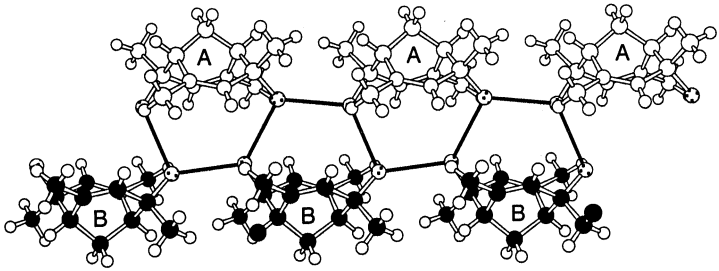


**FIGURE 5** The racemic staircase-ladder structure formed by dialcohol **4**. Two independent molecules (A and B) are contained in the asymmetric unit of this crystal structure. The A strand comprises **4** molecules of one handedness, and the B strand those of the opposite handedness. The same designators as Figure 3 apply here.



chain, and cyclic $(O\text{-}H)_4$ structures [17]. There is considerable evidence that steric factors play a major role in which motif is adopted [17,18].

For monoalcohols Brock and Duncan [18] have discussed how these molecules can form fully hydrogen bonded chains through use of translation, glide planes, or $2_1$ screw axes. Bulkier monoalcohols tend to surround 3, 4, or 6-fold screw, or rotation-inversion axes instead. Similar packing principles operate amongst dialcohol molecules including those discussed here. The new dialcohol 'exceptions' reported here represent ways of adjusting the steric packing without having to finally abandon the staircase-ladder construction.

## CONCLUSIONS

We have shown that dialcohols, encompassing a considerable range of molecular structures, can form two types of double-stranded ladder structure. These hydrogen bonded staircase- and step-ladders assemble with definite enantiomeric and symmetry preferences. For example, all cases of the staircase-ladder structure (within the limits of our CSD survey) involved molecules of only one enantiomer surrounding a $2_1$ screw axis.

New examples of ladder-forming dialcohols can be synthesised with reasonable probability of success and this work has uncovered new variants of staircase-ladder assembly. While racemic **3** underwent self resolution to achieve the customary staircase-ladder arrangement, this dialcohol can also form lattice inclusion compounds where the two strands are enantiomerically pure but of opposite handedness.

Furthermore, the staircase-ladder of dialcohol **4** accommodates two crystallographically independent molecules within its structure. These new and atypical arrangements permit fine-tuning of steric crowding and retention of the ladder structure albeit of a modified type.

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