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Self-assembly of *cis*- and *trans*-cyclic-1,2-diols. Supramolecular synthon equivalence between *cis*-1,2-diols and primary amides

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Abstract

In spite of the fact that the self-assembly of compounds containing hydroxyl group has been enormously documented in the literature, our studies with aliphatic cyclic diols have offered the unique opportunity to examine the self-assembly of *gauche* and *anti* forms of ethylene glycol. Whereas the *cis*-diols are found to form dimers that infinitely assemble further to yield tapes, the *anti*-diols are found to form linear chains that link up further to yield molecular tapes. Notably, both the isomers lead to molecular tapes, which have attracted immense attention since the inception of self-assembly for controlling molecular organization. Quite remarkably, the self-assembly observed with *cis*-diols establish a formal equivalence between supramolecular synthons associated with *cis*-1,2-diols and primary amides. Although the assembly of diols is akin to the tape structure adopted by primary amides, we prefer to view the association of diols as a ladder. The structures of *5-cis* and *8-cis* are both step-ladder assemblies. That formed by *5-trans* is a new variant termed as rope-ladder assembly. The ring motifs observed in the crystal packing suggest for further scope in exploiting the polyhydroxyl compounds for self-assembly in a predictive manner. © 2005 Elsevier B.V. All rights reserved.

Keywords: Crystal structure; Self-assembly; Cyclic-1,2-diols; Step-ladder; Rope-ladder

1. Introduction

Crystal engineering deals with understanding of intermolecular interactions that control the crystal packing and exploitation of such knowledge to engineer molecules in a predictive manner to obtain materials with a predefined function [1]. In this regard, the directionality and strength associated with hydrogen bonds have been reliably exploited to control the molecular organization of molecules [2]. Indeed, a variety of association motifs/synthons [3] that occur reliably in the crystal packing have been identified for a variety of functional groups, [3,4] and search for new and novel motifs that decisively control the crystal packing continues to be of significant contemporary interest.

Insofar as the hydroxyl (–OH) functionality is concerned, there are a variety of ways that the molecules containing a hydroxyl group may exploit hydrogen bonds [5–8]. Given the fact that this functionality contains donor hydrogen

and acceptor oxygen, one can anticipate a minimum of two hydrogen bonds. The analysis of the crystal structures of hydroxyl group containing solid compounds has shown that they form, unless hindered, hydrogen-bonded aggregates mostly via rings, helices and chains [5,6]. Closed dimers akin to carboxylic acids [9] are observed only rarely (approximately only 2% of the crystal structures) [5]. Our recent work [10] involving the helical self-assembly of a norbornene based 1,2-dicarboxylic acid containing a noninteracting, yet bulky hydrophobic trimethylsilyl group at the 7th position prompted us to explore in a similar manner the self-assembly of 1,2 diols. In particular, we were motivated to unravel the preferred pattern of association for the hydroxyl functionalities that are located on vicinal carbons. Indeed, the 1,2-diols may be frozen in either ‘*gauche*’ or ‘*anti*’ conformation by causing them to be a part of cyclic systems. Therefore, we considered the assembly of such systems quite interesting to contrast between the self-assembly of *gauche* and *anti* forms of representative ethylene glycol. Accordingly, we targeted the crystal structure determinations of *cis*- and *trans*-1,2-diols of medium and large-membered cyclic systems to draw contrast between their packing and examine the role of

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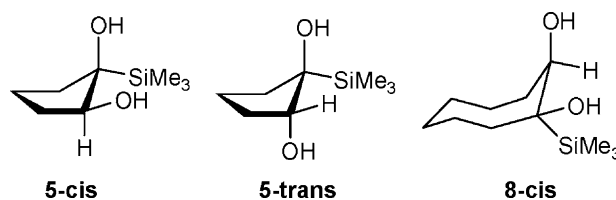


Chart 1.

Table 1
The crystal data for **5-cis**, **5-trans** and **8-cis** diols

Empirical formula	C8 H18 O2 Si	C8 H18 O2 Si	C11 H24 O2 Si
Formula weight	174.31	174.31	216.39
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system, space group	Monoclinic, <i>C2/c</i>	Triclinic, <i>P-1</i>	Orthorhombic, <i>Pbn2₁</i>
Unit cell dimensions	$a=21.5441(15)$ Å $b=9.0715(6)$ Å $c=10.9956(7)$ Å $\beta=100.828(2)^\circ$	$a=8.658(4)$ Å; $\alpha=63.67(1)^\circ$ $b=11.348(6)$ Å; $\beta=70.17(1)^\circ$ $c=12.717(6)$ Å; $\gamma=85.48(1)^\circ$	$a=9.794(5)$ Å $b=10.884(5)$ Å $c=25.309(1)$ Å
Volume	$2110.7(2)$ Å ³	$1049.6(2)$ Å ³	$2697.9(2)$ Å ³
Z, Calculated density	8, 1.097 g/cm ³	4, 1.103 g/cm ³	8, 1.065 g/cm ³
Absorption coefficient	0.181 mm ⁻¹	0.182 mm ⁻¹	0.153 mm ⁻¹
<i>F</i> (000)	768	384	960
Crystal size	$0.3 \times 0.2 \times 0.1$ mm ³	$0.3 \times 0.2 \times 0.1$ mm ³	$0.3 \times 0.2 \times 0.1$ mm ³
Theta range for data collection	1.92 – 23.46°	1.90 – 23.28°	1.61 – 23.27°
Reflections collected/unique	4247/1514 [<i>R</i> (int)=0.1558]	3369/2105 [<i>R</i> (int)=0.0448]	10615/2948 [<i>R</i> (int)=0.1065]
Completeness to theta=23.46	97.2%	69.4%	99.9%
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	1514/0/108	2105/0/191	2948/1/250
Goodness-of-fit on <i>F</i> ²	0.916	1.045	1.190
Final <i>R</i> indices [<i>I</i> >2σ(<i>I</i>)]	<i>R</i> 1=0.0679, <i>wR</i> 2=0.1525	<i>R</i> 1=0.0531, <i>wR</i> 2=0.1272	<i>R</i> 1=0.0833, <i>wR</i> 2=0.1792
<i>R</i> indices (all data)	<i>R</i> 1=0.0866, <i>wR</i> 2=0.1637	<i>R</i> 1=0.0755, <i>wR</i> 2=0.1445	<i>R</i> 1=0.1269, <i>wR</i> 2=0.2053
Largest diff. peak and hole	0.348 and -0.373 e Å ⁻³	0.404 and -0.365 e Å ⁻³	0.309 and -0.209 e Å ⁻³
Extinction coefficient	0.1637	0.0004(19)	0.1(4)

trimethylsilyl (TMS) group as well. Herein, we discuss the self-assembly of *cis*- and *trans*-1-trimethylsilylcyclopentane 1,2-diol (**5-cis** and **5-trans**) and *cis*-1-trimethylsilylcyclooctane 1,2-diol (**8-cis**).

2. Experimental

All the diols, viz. **5-cis**, **5-trans** and **8-cis**, were available from our previous synthetic studies [12]. The crystals of **5-cis** and **5-trans** were crystallized using chloroform solvent and that of **8-cis** were grown using methanol with slight warming. The crystallographic intensity data for all the crystals were collected on Siemens Smart CCD area detector. The crystal data details for all the three compounds in Chart 1 are given in Table 1.

3. Results and discussion

The crystals of **5-cis** were found to be monoclinic with space group: *C2/c*. Fig. 1 shows the molecular structure of the *cis*-diol. The 5-membered ring exists in a perfect envelope conformation with TMS group occupying

the equatorial position. The torsion angle between the two hydroxyl groups is 51.8° . Fig. 2 shows the crystal-packing diagram of **5-cis**. As can be seen, the *cis*-diols exploit hydrogen bonding between the hydroxyl groups. The centrosymmetrically related molecules form dimers by exploiting two hydrogen bonds. The dimers further associate via additional two hydrogen bonds to form linear tapes along the *c*-axis. Such a linear association is further facilitated in the crystal lattice by the hydrophobic association of the aliphatic moiety. Undoubtedly, the crystal packing is controlled by the self-assembly of hydroxyl groups. This assembly is termed as step-ladder where

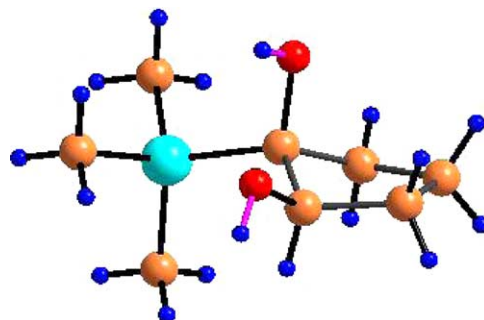


Fig. 1. The molecular structure of *cis*-cyclopentane-1,2-diol (**5-cis**).

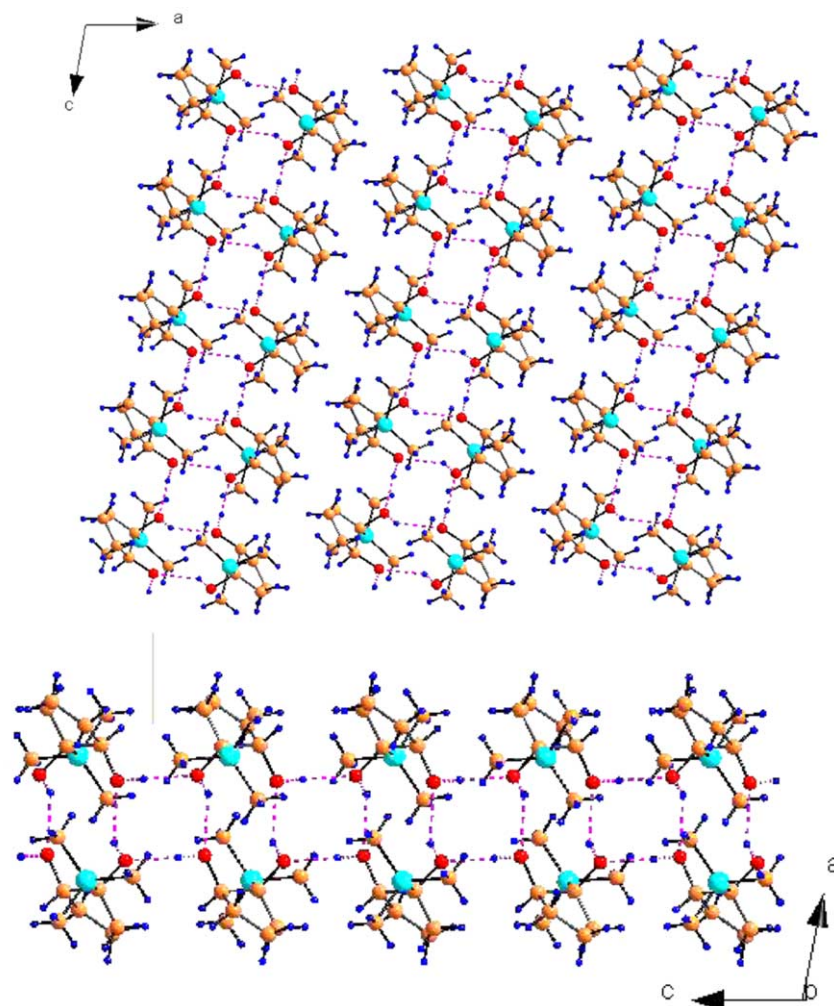


Fig. 2. The crystal packing diagram of *cis*-cyclopentane-1,2-diol (**5-cis**). The bottom diagram exhibits typical assembly of the molecules via O–H⋯O hydrogen bonds.

molecules are connected by (O–H)₄ cycles of hydrogen bonds [7,8]. The geometrical parameters associated with the hydrogen bonds are given in Table 2. The $D_{O\dots O}$ and $d_{O-H\dots O}$ distances suggest that the strengths of the hydrogen bonds are moderate [2d].

The *trans*-cyclopentane-1,2-diol **5-trans** was found to crystallize in the space group *P*-1 with two independent molecules in the unit cell (Fig. 3). Here again, the 5-membered rings in both the molecules adopt a perfect

envelope conformation with the trimethylsilyl groups occupying the equatorial positions. The torsion angles between the *trans* hydroxyl groups are 166.23 and 165.58° in molecules A and B, respectively. Interestingly, the two molecules in the asymmetric unit cell exist as a hydrogen-bonded pair. As one may anticipate, the two molecules associate as a linear chain along the *b*-axis (Fig. 4). Thus, the connectivity is more like a zigzag chain involving the pattern: —O1A–O2A—O2B–O1B—O1A–O2A—O2B–O1B—.

Table 2

The geometrical parameters for the hydrogen bonds in **5-cis**, **5-trans** and **8-cis** diols

Diol	Interacting atoms	Symmetry	$D_{O\dots O}/\text{\AA}$	$d_{H\dots O}/\text{\AA}$	$\theta_{O-H\dots O}/^\circ$
5-cis	O1–H⋯O2	$-x, 1-y, 1-z$	2.854 (2)	2.198 (1)	146.0 (3)
	O2–H⋯O1	$x, 1-y, -0.5+z$	2.774 (1)	1.861 (1)	171.9 (3)
5-trans	O1B–H⋯O1A	x, y, z	2.856 (5)	2.124 (3)	145.47 (2)
	O1A–H⋯O2B	$1-x, 1-y, -z$	2.765 (3)	1.956 (2)	161.59 (2)
	O2A–H⋯O2B	$x, -1+y, z$	2.907 (5)	2.121 (3)	155.62 (2)
8-cis	O1A–H⋯O2B	x, y, z	2.880 (6)	2.167 (5)	145.42 (1)
	O1B–H⋯O2A	x, y, z	2.897 (7)	2.186 (6)	145.22 (1)
	O2A–H⋯O1A	$1.5-x, 0.5+y, z$	2.798 (8)	2.163 (3)	134.38 (1)
	O2B–H⋯O1B	$1.5-x, -0.5+y, z$	2.853 (13)	2.175 (2)	140.09 (1)

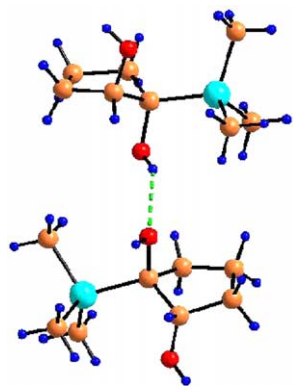


Fig. 3. The molecular structures of two independent hydrogen-bonded molecules of the anti-cyclopentane-1,2-diol (**5-trans**).

These linear chains further link up by utilizing the hydrogen of O1A and the lone pair of O2B to form one-dimensional tapes. In other words, it is the hydrogen-bonded linear chains that laterally assemble further to form a ladder. In this process, the hydrogen attached to O2B remains free without any hydrogen bonding, while the oxygen atom serves to accept two hydrogen bonds at the same time; thus, the geometry around this oxygen is tetrahedral. It is of interest to

note that the *trans*-diol that typically represents ethylene glycol in its *anti* conformation forms a 14-membered ring, which is heretofore, unknown for the self-assembly involving the hydroxyl group. This hydrogen bonded connectivity between the two strands is quite different and unusual. This assembly formed by **5-trans** is a new variant, different from the step-ladder and the staircase-ladder assemblies observed earlier [7,8]. This new variant is termed as rope-ladder assembly [11].

The *cis*-cyclooctane-1, 2-diol, **8-cis** was found to crystallize in orthorhombic crystal system (space group: $Pbn2_1$). The asymmetric unit cell contains two independent molecules that are interestingly hydrogen bonded (Fig. 5). The medium-sized rings in both the molecules are found to adopt pseudo-chair conformations. The two hydrogens that are left nonhydrogen-bonded in the dimer associate further like in the case of **1** to form a linear tape, akin to step-ladder assembly observed in **5-cis**. The geometrical parameters for the hydrogen bonds are given in Table 2. The packing depicted in Fig. 6 typically resembles that of the 5-membered ring counterpart **5-cis**, with the exception that the dimeric pair in the latter is formed between centrosymmetrically related molecules, while it is between

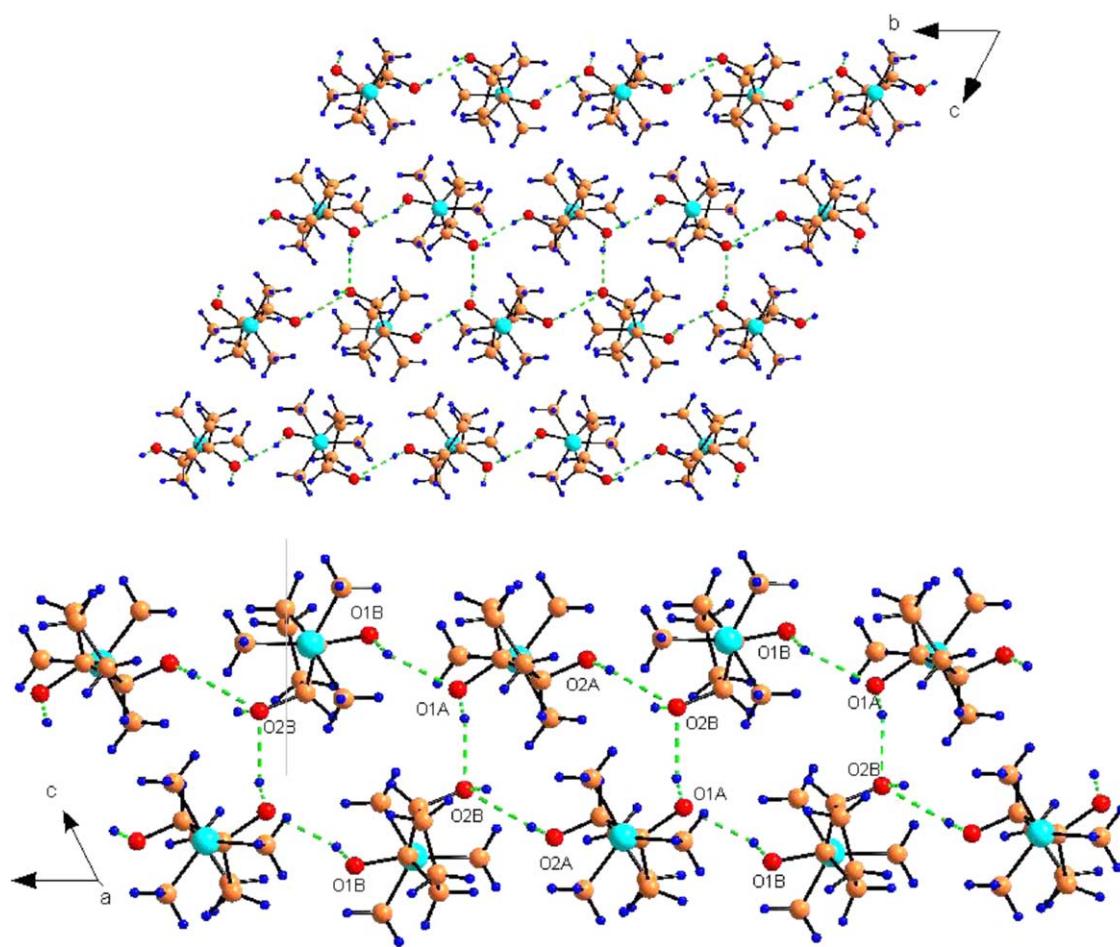


Fig. 4. The crystal packing diagram of anti-cyclopentane-1,2-diol (**5-trans**). The bottom diagram shows how the linear chains are linked up to form tape structures.

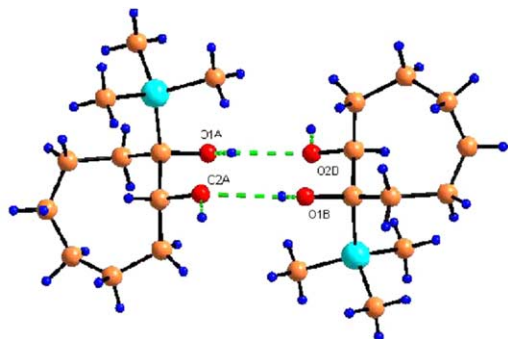


Fig. 5. The molecular structures of the two independent hydrogen-bonded *cis*-octane-1,2-diol (**8-cis**).

two independent molecules in the former. Further, one observes, as in the previous cases, hydrophobic association of the aliphatic moiety. The hydrogen bonding and the hydrophobic association control the crystal packing.

Both the *cis*-1,2-diols, viz. **5-cis** and **8-cis**, are found to undergo self-assembly with virtually no perceptible differences in their crystal packing. In both cases, the

dimerization leads to a readily recognizable hydrogen-bonded-ring motif of the type: $R_2^2(10)$ [14]. Further assembly of these dimers as shown in Fig. 7 leads to a molecular ladder via the motif: $R_4^4(8)$. It is quite instructive to compare the observed pattern of self-assembly for the *cis*-diols with that known for primary amides, [13–16] see Fig. 7. While it is $R_2^2(8)$ motif that brings about the dimeric association in the latter, the $R_2^2(10)$ motif accomplishes a similar job in the case of *cis*-1,2-diols. In a similar manner, the C(5) chain brings about the hydrogen-bonded aggregation into a tape, while it is the C(4) chain in amides. Thus, it emerges from a simple comparison that the *cis*-1,2-diols serve as supramolecular synthon equivalents to those of primary amides. That the crystal packing of *anti*-1, 2-diol is indeed distinctly different is suggested by the X-ray crystal structure of **5-trans**. In this case, the two hydrogen-bonded molecules in the asymmetric unit cell undergo self-assembly to yield a one-dimensional chain. Notably, the one-dimensional hydrogen-bonded chains running in anti-parallel direction link up further through two hydrogen bonds via the ring motif: $R_4^4(14)$, where two of the oxygen

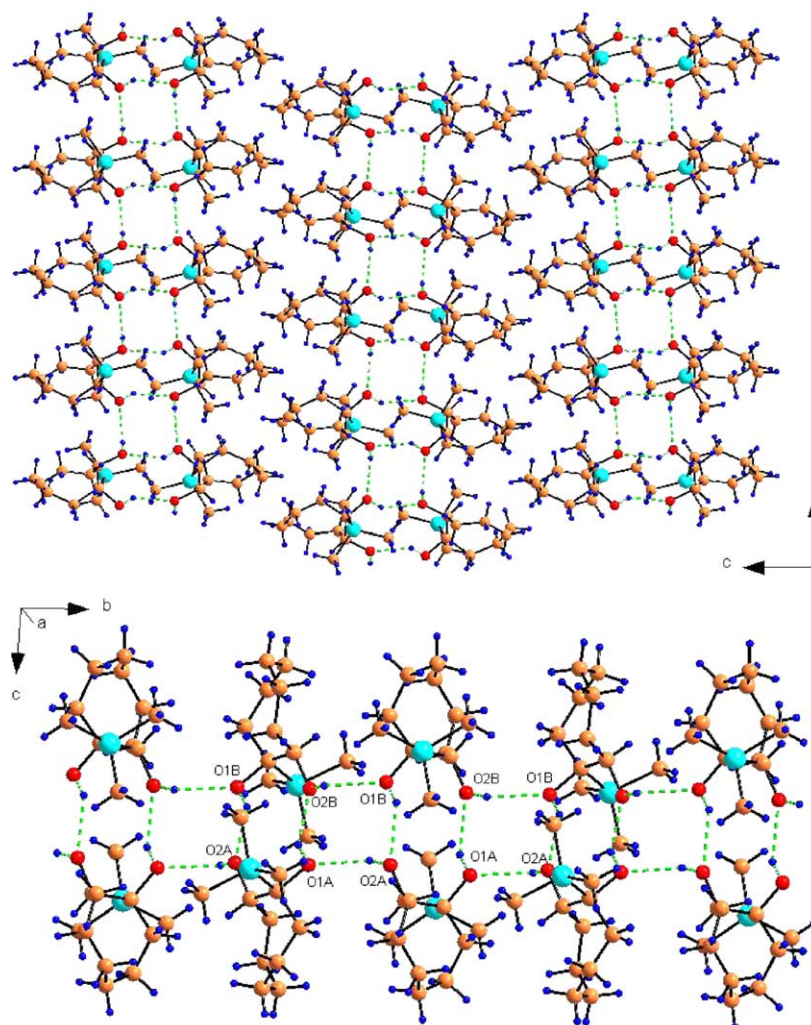


Fig. 6. The crystal packing diagram of *cis*-cyclooctane-1,2-diol (**8-cis**). The bottom picture shows the linkage of the dimers.

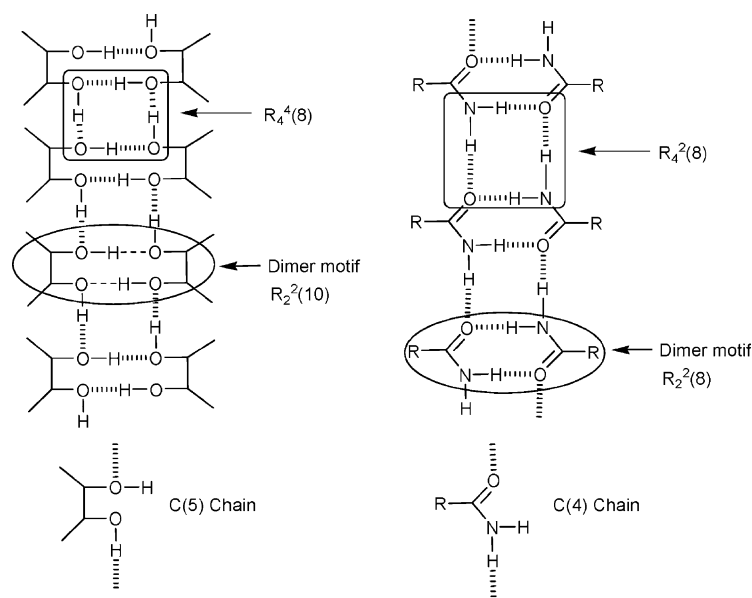


Fig. 7. The dimeric motifs of the carboxylic acids and hydroxyl groups. The observed self-assembly of *cis*-1,2-diols **5-cis** and **8-cis**. For comparison, the known motif for primary amides is shown on the right. Observe the formal equivalence of the self-assembly for *cis*-1,2-diols and primary amides.

atoms of the ring motif serve to accept two hydrogen bonds simultaneously. Such an assembly leads to a molecular ladder termed rope-ladder.

In summary, despite the fact that the self-assembly of compounds containing hydroxyl group has been enormously documented in the literature, our studies with aliphatic cyclic diols have offered the unique opportunity to examine the self-assembly of *gauche* and *anti* forms of ethylene glycol. So far, two distinct types of double stranded ladder structures termed as step-ladders and staircase-ladders are known, whereas, the *cis*-diols are found to form dimers that infinitely assemble further to yield step-ladder, the *anti*-diols are found to form linear chains that link up further to yield a different and unusual assembly. This novel assembly is termed rope-ladder. Notably, both the isomers self-assemble into ladder structures which have attracted immense attention since the inception of self-assembly for controlling molecular organization. Quite remarkably, the self-assembly observed with *cis*-diols establish a formal equivalence between supramolecular synthons associated with *cis*-1,2-diols and primary amides. The ring motifs observed in the crystal packing suggest for further scope in exploiting the polyhydroxyl compounds for self-assembly in a predictive manner.

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