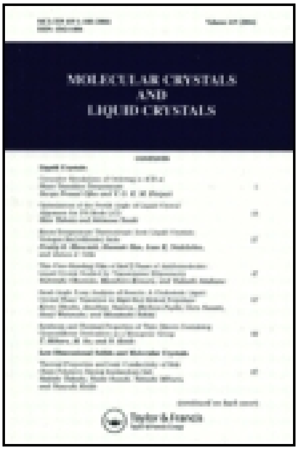

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Increasing the Landscape of Structural Motifs in Co-crystals of Resorcinols with Ditopic Aromatics: A One-dimensional π-Stacked Hydrogen-Bonded Polymer Involving a Phenanthroline

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Version of record first published: 21 Dec 2006

To cite this article: Tomislav Friščić & Leonard R. MacGillivray (2006): Increasing the Landscape of Structural Motifs in Co-crystals of Resorcinols with Ditopic Aromatics: A One-dimensional π-Stacked Hydrogen-Bonded Polymer Involving a Phenanthroline, Molecular Crystals and Liquid Crystals, 456:1, 155-162

To link to this article: http://dx.doi.org/10.1080/15421400600788666

Mol. Cryst. Liq. Cryst., Vol. 456, pp. 155–162, 2006
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400600788666

Increasing the Landscape of Structural Motifs in Co-crystals of Resorcinols with Ditopic Aromatics: A One-dimensional π-Stacked Hydrogen-Bonded Polymer Involving a Phenanthroline

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*Co-crystals involving 4,6-dichlororesorcinol (4,6-diCl-res) and 2,9-phenanthroline (2,9-phen) of composition 2(4,6-diCl-res)·2(2,9-phen)·(nitromethane) (**1**) reveal a previously unobserved one-dimensional structural motif that involves a π-stacked columnar polymer held together by $O-H\cdots N$ hydrogen bonds. Each resorcinol participates in short $Cl\cdots O$ contacts and $Cl\cdots Cl$ forces along the polymer backbone. The included nitromethane solvent molecules pack in columns held together by $C-H\cdots O$ forces.*

Keywords: co-crystal; hydrogen bonds; phenanthroline; polymer; resorcinol

INTRODUCTION

Extensive efforts to understand factors that govern the arrangements of molecules in organic solids have led to significant advances in the design and construction of functional solid-state materials [1]. Efforts to control organic solid-state reactivity [2] have been recognized as important for the construction of solids that serve as switches [3], nanomotors [4] and/or exhibit deformability [5]. From the standpoint of synthetic chemistry, control of solid-state reactivity has recently led to the deliberate construction of hydrocarbons in the form of cyclophanes and ladderanes [6,7], as well as natural products [8]. With such advances now achieved, the potential to build reactive and functional

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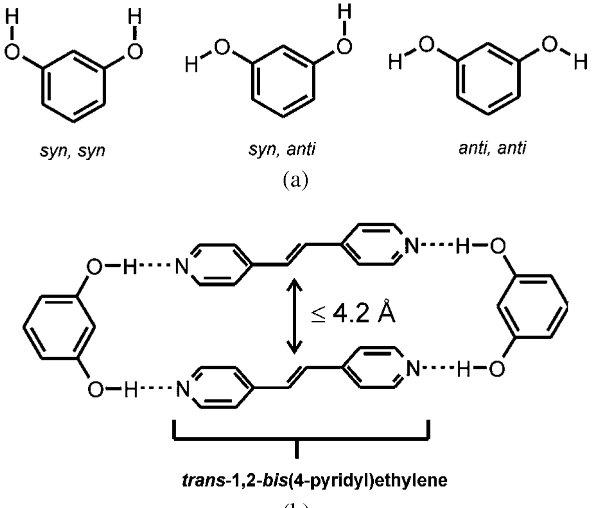
We are grateful to the National Science Foundation (CAREER Award, LRM, DMR-0133138) for partial support of this work.

Address correspondence to Leonard R. MacGillivray, University of Iowa Chemistry Department, 305 Chemistry Building, Iowa City, IA, 52242-1294, USA. E-mail: len-macgillivray@uiowa.edu organic solid-state materials has experienced new and exciting levels [9], which provide an impetus to develop structure motifs that define the organization of molecules within such solids [10].

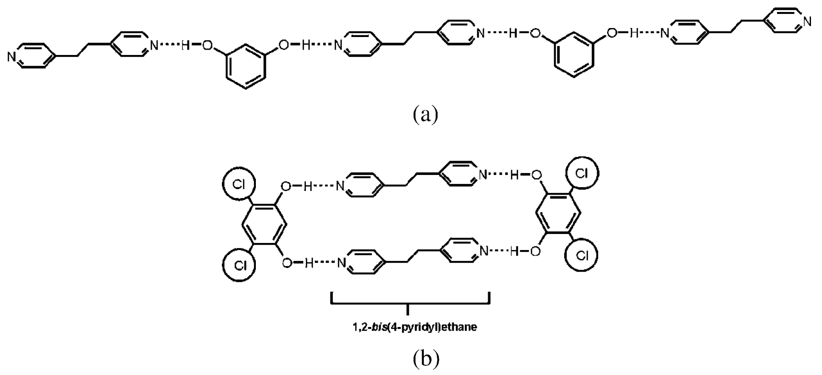
In this context, we have shown that ditopic molecules, in the form of resorcinols, can be used to assemble ditopic aromatics within co-crystals, of general composition (resorcinol)·(aromatic), that consist of finite molecular assemblies held together by O−H···N hydrogen bonds [11] (Scheme 1). In these assemblies, each resorcinol adopts a *syn,syn* conformation (Scheme 1a) [12] that juxtaposes the aromatics at a close separation. We have shown that this approach can be used to organize ditopic olefins in finite assemblies, of composition 2(resorcinol)·2(*trans*-1,2-bis(4-pyridyl)ethylene), in positions suitable for intermolecular [2 + 2] photodimerizations (Scheme 1b) [9,11]. We have also shown that the conformational flexibility of the resorcinol can lead to co-crystals involving a 1-dimensional (1-D) hydrogen-bonded polymer [13], of composition (4,6-diCl-res)·(4,4′-bis(4-pyridyl)ethane) (where: 4,6-diCl-res = 4,6-dichlororesorcinol), wherein the diol adopts an *anti,anti* conformation. In this 1D framework, the polymer is propagated approximately parallel to the direction of the O−H···N bonds (Scheme 2a). We have demonstrated that the formation of the 1D polymer can be controlled *via* covalent preorganization [14] in which sterically demanding *ortho* substituents force the resorcinol in the



(a)

(b)

SCHEME 1



SCHEME 2

syn,syn conformation and the assembly process to form a finite structure (Scheme 2b) [13].

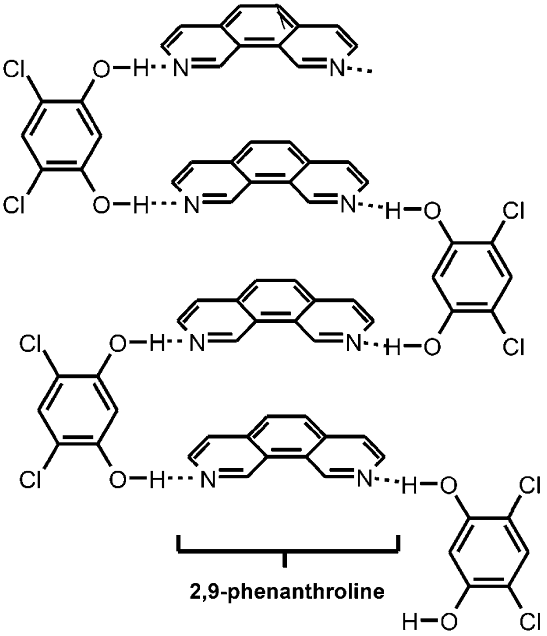
In this report, we wish to describe a third structural motif in co-crystals involving a resorcinol and ditopic aromatic. This third motif has been obtained serendipitously during a co-crystallization of 4,6-diCl-res with *cis*-1,2-bis(4-pyridyl)ethylene, whereupon the olefin has undergone an oxidative cyclization to give 2,9-phenanthroline (2,9-phen) [15]. The co-crystals, of composition 2(4,6-di-Cl-res)·2(2,9-phen)·(nitromethane) **1**, consist of a 1D π-stacked polymer held together by O–H···N hydrogen bonds (Scheme 3). In this 1D framework, the resorcinol adopts a *syn,syn* conformation. Importantly, the polymer forms despite the fact that the diol possesses *ortho* substituents and adopts the *syn,syn* conformation. The new motif attests to an increasing level of structural diversity encountered in such molecular solids.

EXPERIMENTAL

All compounds and solvents, unless otherwise stated, were commercially available from Sigma-Aldrich. *Cis*-1,2-*bis*(4-pyridyl)ethylene was obtained from *trans*-1,2-*bis*(4-pyridyl)ethylene *via* a literature report [16].

Preparation of 2(4,6-diCl-res)·2(2,9-phen)·CH_3NO_2 (1)

A heated, supersaturated solution of 4,6-diCl-res (0.36 g) and *cis*-1,2(4-pyridyl)ethylene (0.36 g) (1:1 molar ratio) in nitromethane was allowed to cool and stand for a period of approximately 8 hours. The solution produced colorless prisms of composition



SCHEME 3

2(4,6-diCl-res)·2(2,9-phen)·(nitromethane) **1**(0.60 g; yield: 77%). The formulation of **1** was confirmed *via* single-crystal X-ray diffraction.

Single-Crystal X-ray Crystallography

X-ray crystallographic data for **1** were collected on a Nonius Kappa CCD diffractometer equipped with a graphite monochromator using MoKα radiation. The compound crystallized in the triclinic system, space group $P\bar{1}$, with unit cell parameters $a = 8.601(1)$ Å, $b = 12.946(1)$ Å, $c = 17.298(2)$ Å, $\alpha = 73.909(5)°$, $\beta = 84.225(5)°$, $\gamma = 71.317(5)°$ and $V = 1753.02(4)$ Å^3 (unique reflections: 7642, reflections with having $I \geq 2\sigma(I)$:5858). After anisotropic refinement of all non-hydrogen atoms, aromatic and hydroxyl hydrogen atoms were placed in idealized positions and allowed to ride on the atom to which they are attached. The structure refined to a final R value of 0.044.

RESULTS AND DISCUSSION

An ORTEP perspective of **1** is shown in Figure 1. The asymmetric unit consists of five molecules: two crystallographically independent

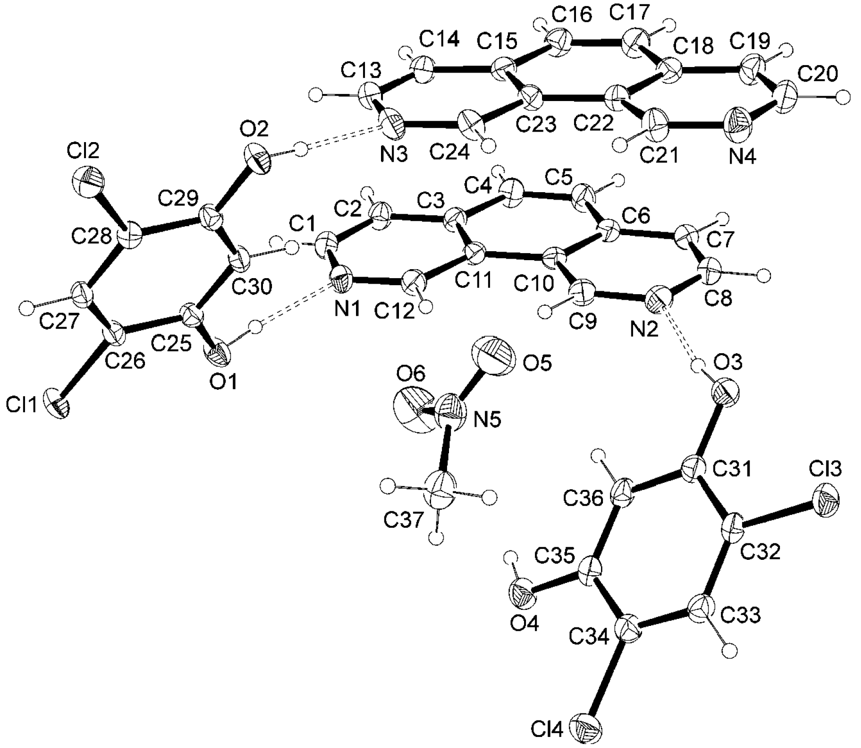
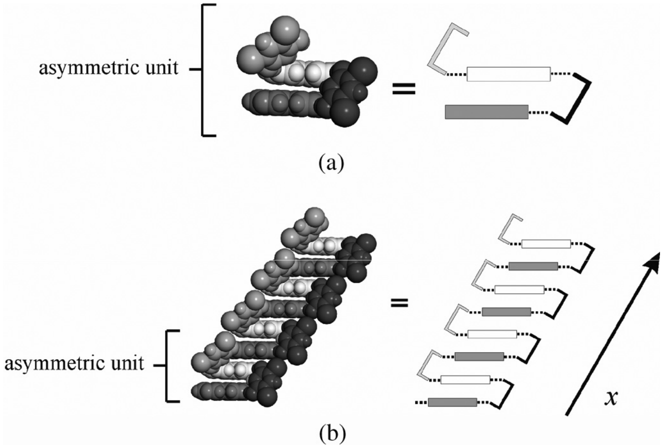


FIGURE 1 ORTEP perspective of the asymmetric unit of **1**. Non-hydrogen atoms are shown as ellipsoids at 30% probability level.

molecules of 2,9-phen, two crystallographically independent molecules of 4,6-diCl-res, and a single molecule of nitromethane. As shown in Figure 2, the resorcinol and phenanthroline molecules of the asymmetric unit have assembled *via* O–H···N hydrogen bonds (N···O separations (Å): O(1)···N(1) 2.722(2), O(2)···N(3) 2.694(2), O(3)···N(2) 2.711(2), O(4)···N(4)^{i} 2.722(3); symmetry operator *i*: $x-1$, y, z) to form a 1D polymer that runs parallel to the crystallographic x-direction. In this arrangement, each resorcinol adopts a *syn,syn* conformation such that the two independent phenanthrolines, which participate in offset face-to-face π-π forces (centroid···centroid: 4.03 Å), lie juxtaposed to the diol. As a consequence of these forces, the resorcinol and phenanthroline units (centroid···centroid: 5.15 Å) form polar 1D stacked columns, which repeat in an *ABAB* fashion, that are propagated at an angle of approximately 55° with respect to the plane of the π-stacking. Thus, in contrast to (4,6-diCl-res)·(4,4′ -bis(4-pyridyl)ethane) [13], the



(a)
(b)

FIGURE 2 Schematic representation of: (a) the repeat unit of the polymer; (b) the structure of a single polymer of **1**.

hydrogen bonds of **1** run approximately perpendicular to the direction of the 1D array.

As shown in Figure 3, the resorcinol molecules of each 1D array of **1** assemble along the backbone of the hydrogen-bonded polymer *via* a combination of Cl···O (Cl(1)···O2^{i}, 2.87 Å) and Cl···Cl (Cl(2)···Cl(1)^{ii}, 4.24 Å, Cl(3)···Cl(4)^{ii}, 3.88 Å; symmetry operator *ii*: $x+1$, y, z) forces [17–19] (Fig. 3a). Neighboring columns of **1** assemble *via* Cl···Cl interactions (Cl···Cl separations (Å): Cl(1)···Cl(2)^{iii} 3.85, Cl(1)···Cl(4)^{iv} 3.81, Cl(2)···Cl(3)^{v} 3.97, Cl(2)···Cl(2)^{vi} 4.20 Å; symmetry operators *iii*: $-x$, $2-y$, $-z$; *iv*: $-x$, $1-y$, $1-z$; *v*: $1-x$, $1-y$, $1-z$; *vi*: $1-x$, $2-y$, $-z$) (Fig. 3b) and are separated by included nitromethane molecules. The solvent molecules are stacked in a head-to-tail fashion and participate in C–H···O forces with the resorcinol and phenanthroline units of the 1D polymeric array (C···O separations: O(6)···C(12) 3.42 Å, C(37)···O(4) 3.48 Å, O(6)···C(21)^{i} 3.43 Å, C(37)···O(4)^{iv} 3.47 Å, O(5)···C(37)^{v} 3.48 Å) (Fig. 3c) [20].

CONCLUSION

We have described the discovery of a third structural motif involving co-crystals based on a resorcinol and ditopic aromatic. The motif consists of a 1D π-stacked array that is held together by O–H···N

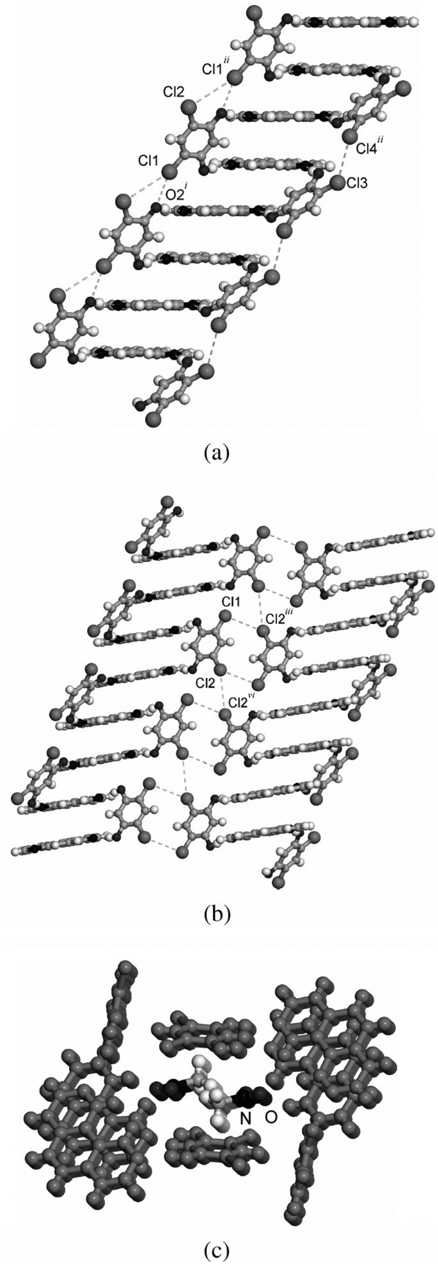


FIGURE 3 Ball-and-stick representations of the extended structure of **1**: (a) stacked column, (b) the two different sets of Cl$\cdots$Cl interactions, and (c) a view of the included CH_3NO_2 solvent molecules approximately parallel to the crystallographic *x*-axis (N and O atoms of solvent molecules labeled for clarity).

hydrogen bonds, as well as Cl···O and Cl···Cl forces. Work is currently underway to establish conditions for the reliable construction of π-stacked solids based on the 1D motif. In principle, the motif may be used to direct chemical reactivity in the crystalline state.

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