Molecular Crystals and Liquid Crystals

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

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Version of record first published: 18 Oct 2010

To cite this article: Naoto Hayashi, Kumiko Yamaguchi & Kiyoshi Matsumoto (2002): Packing Structure of Phenol Trimers, Molecular Crystals and Liquid Crystals, 390:1, 5-10

To link to this article: http://dx.doi.org/10.1080/15421400390193431

Mol. Cryst. Liq. Cryst., Vol. 390, pp. 5–10

1542-1406/03 $12.00 + .00
DOI: 10.1080/15421400390193431

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PACKING STRUCTURE OF PHENOL TRIMERS

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*2,2′:6′,2″-Terphenyl-1,1′,1″-triol (**1**), a possible supramolecular synthon, has been synthesized. Its X-ray structure shows that **1** forms a hydrogen-bonded cyclic dimer which was expected. On the other hand, its 4,4′,4″-trimethyl derivative (**2**) gave 1:1 ethanol complex, (**2**)(ethanol), in which not a cyclic dimer but a helical hydrogen bond network with interposition of ethanol is observed.*

Keywords: X-ray structure; phenol trimer; terphenyl; hydrogen bond

INTRODUCTION

Control of crystal structure is difficult in general [1]. So, in order to design crystals consisting of desired molecular arrangement, a particular intermolecular interaction is often introduced. Such interactions are called supramolecular synthons [2,3].

Carboxylic acids are known to be excellent supramolecular synthons [4,5]. These acids usually form the hydrogen-bonded dimer, and the other forms of hydrogen bond network (*e.g.*, infinite catemer) have been rarely encountered. Owing to this strong preference, these acids are frequently used for the purpose of crystal engineering [6,7]. However, these acids are not always useful, since they are not applicable when strong base is present or electron-withdrawing substituent is undesirable. Here, we have focused our attention on phenol trimers bearing meta-terphenyl backbone as a possible supramolecular synthon. When all hydroxyl groups participate in intramolecular hydrogen bond, one hydrogen bond donor and one acceptor will be left, which would be used for intermolecular hydrogen bond. If it

Financial support by the Sasakawa Scientific Research Grant and a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology, Japan (90281104) is gratefully acknowledged.

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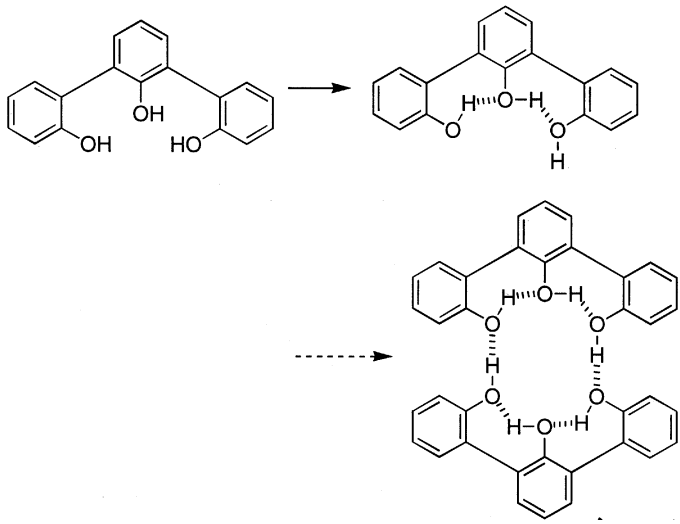
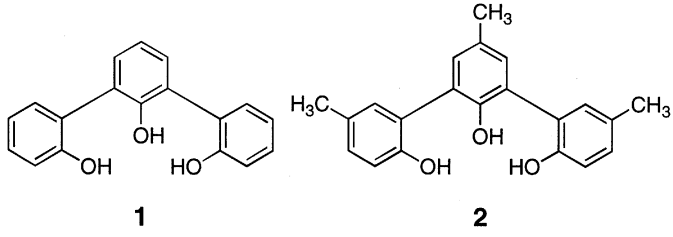


SCHEME 1



1 **2**

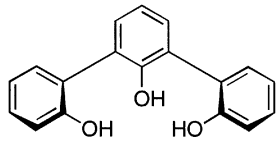
gives a cyclic dimer with a center of symmetry, it can be regarded as an analogue of carboxylic acids (see Scheme 1). Moreover, since phenol is less acidic than carboxylic acid and is an electron-donating group, the phenol trimers will function as a supramolecular synthon even in cases where carboxylic acids are not applicable. In the present paper, we wish to report synthetic methods of phenol trimers **1** and **2**, and their X-ray structure.

RESULTS AND DISCUSSION

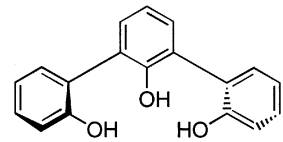
The phenol trimers **1** and **2** were synthesized as follows. 2-Methoxyphenylboronic acid and 2,6-dibromoanisole were coupled by means of

palladium catalyst (Suzuki-Miyaura coupling) to give the precursor of **1**. The precursor of **2** was obtained in a similar manner but from 2-methoxyl-5-methylphenylboronic acid and 2,6-diiodo-4-methylanisole. The obtained precursors were demethylated by boron tribromide to afford **1** and **2** in good yields.

By recrystallization from methanol solution, good crystals of **1** suitable for X-ray diffraction analysis were yielded. Crystal structure of **1** is shown in Figure 1. Both hydroxyl groups on the side aryl moieties are found to lie on the same side with respect to the central benzene ring. This conformer is defined as syn in this work. The torsional angles between adjacent aromatic rings are 56 and 55°. Interatomic distances between oxygen atoms



syn-**1**



anti-**1**

are observed to be 2.93 (O1-O2) and 2.92 Å (O2-O3), which indicate that both pairs of hydroxyl groups are hydrogen-bonded. Tow molecules of **1** are linked by means of hydrogen bond to form the cyclic dimer, as we expected. Interatomic distance between oxygen atoms (O1-O3′) is 2.87 Å.

On the other hand, when **2** was recrystallized from aquaous ethanol, 1:1 complex, (**2**)(ethanol), was obtained. Its X-ray structure is shown in Figure 2. Interestingly, **2** takes anti conformation. Absolute values of dihedral angles are 47 and 47°, which are similar to those of **1**. Intramolecular hydrogen bonds are also observed in 1, in which interatomic distances between oxygens are 2.59 and 2.56 Å for O1-O2 and O2-O3, respectively. It is noted that hydrogen bond network in (**2**)(ethanol) is not the cyclic dimer but a helical one, which is composed of an alternavie arrangement of **2** and ethanol molecules. Interatomic distances between oxygen atoms are 2.72 and 2.59 Å for O1-O(ethanol) and O3-O(ethanol), respectively.

If the helical molecular arrangement found in (**2**)(ethanol) is due to the complexation with ethanol, it is important to determine crystal structure of guest-free **2**. Then we attempted to recrystallize **2** from various solvent including ether, dichloromethane, chloroform, benzene, toluene, hexane, ethyl acetate, and methanol. All solutions mentioned above yielded guest-free **2**, but unfortunately, no good crystal for X-ray analysis was obtained.

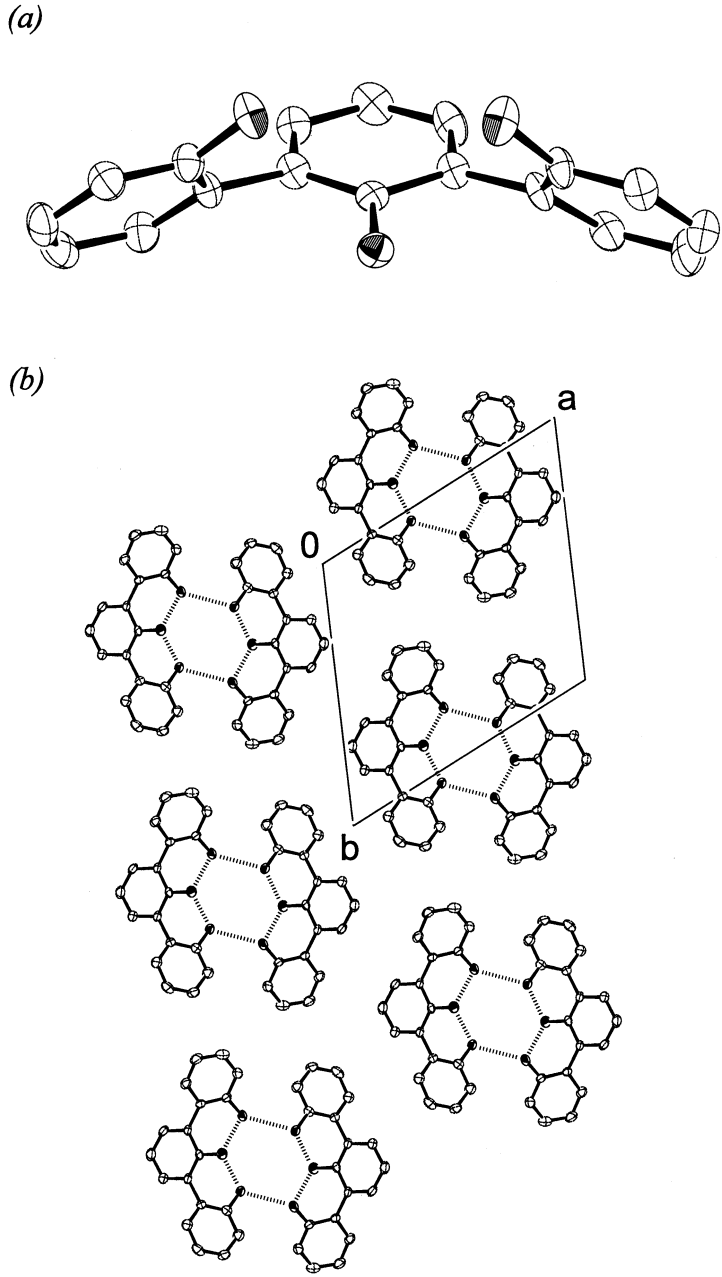


FIGURE 1 X-ray structure of (**1**): molecular structure *(a)* and packing structure *(b)*.

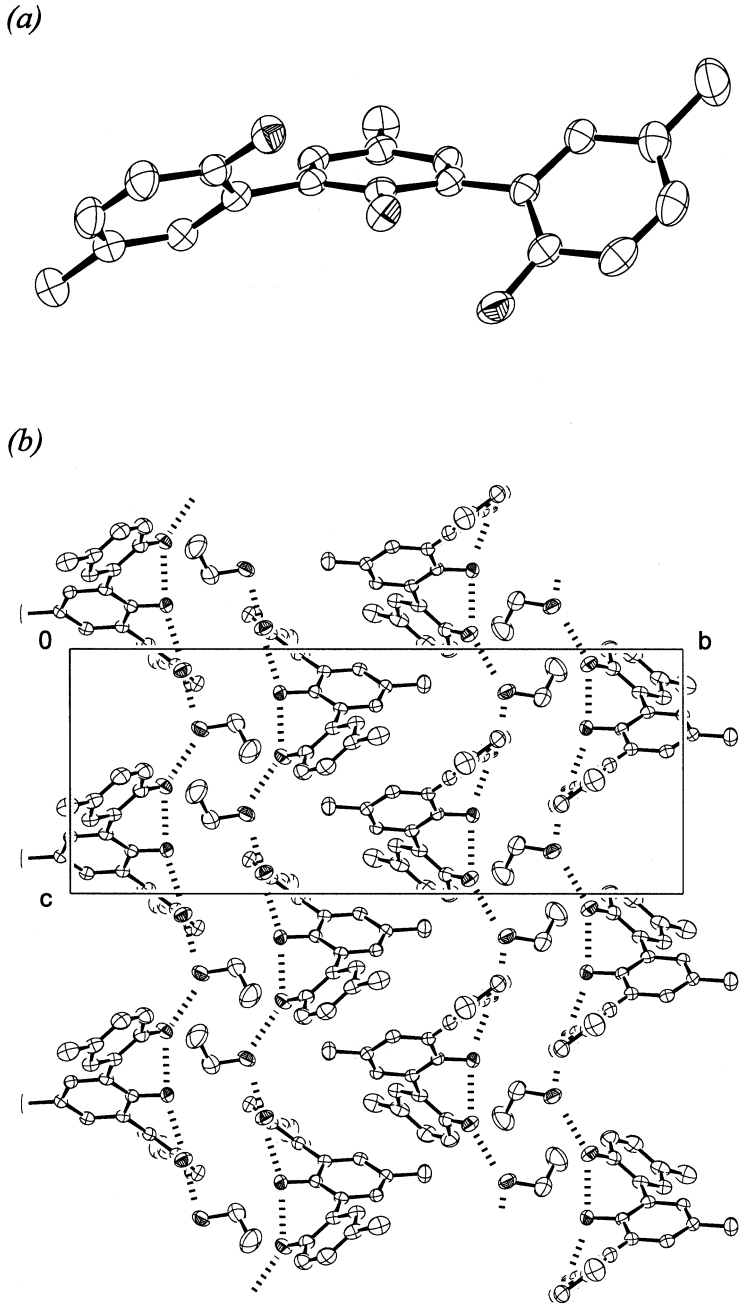


FIGURE 2 X-ray structure of (**2**)(ethanol): molecular structure of **2** *(a)* and packing structure *(b)*.

We also tried to prepare 1:1 ethanol complex of **1**, although no ethanol complex was given.

As mentioned above, the hydrogen-bonded cyclic dimer, which we had expected for phenol trimers, are obtained when they adopt syn conformation, whilst an unexpected helical network is given when anti conformation is taken. If this rule is general, it is important to know how much the difference in energy between syn and anti conformer is. Then we examined AM1 calculation for **1**, and revealed that although syn is more stable, the energetic difference between these conformers is as little as $0.30\,\mathrm{kcal\,mol^{-1}}$. The slight difference may indicate that either conformer can appear.

If only the syn conformer gives the cyclic dimer and the anti conformer affords another form, it appears that phenol trimers can be used in limited cases as a supramolecular synthon. However, note that, in spite of different molecular conformation, a common feature is observed. Namely, in both X-ray structures, hydrophilic and hydrophobic areas are clearly separated. In **1**, layers containing hydrogen bond network and terphenyl are stacked alternatively along c axis. On the other hand, in **2**, from the viewpoint along c axis, the helical hydrogen bond network area is clearly separated from terphenyl moieties area. This finding is reminiscent of crystal structure of clathrates of deoxycholic and cholic acids, and encouraged us to design new host molecules bearing phenol trimer structure. Investigations on crystal structures composed of related compounds are currently underway.

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