AN INFINITE HYDROGEN-BONDED MOLECULAR ASSEMBLY BASED ON CATECHOL AND A BIFUNCTIONAL OLEFIN

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1. ABSTRACT

Catechol (cat) and *trans*-1,2-bis(4-pyridyl)ethylene (4,4'-bpe) form a 1:1 co-crystal, of composition (cat)·(4,4'-bpe) 1, that consists of infinite one-dimensional (1D) undulating chains held together by O-H···N hydrogen bonds. The chains are based on an alternating sequence of five crystallographically independent molecules, two that involve cat and three that involve 4,4'-bpe, and an eight-component repeat unit. The cat molecules adopt an *anti-anti* conformation, while the olefins adopt either a co-planar or twisted conformation. The chains self-assemble *via* a combination of face-to-face π-π interactions, C-H···π forces, and C-H···O hydrogen bonds.

2. INTRODUCTION

The engineering of molecular crystalline solids with components assembled in predefined geometries and packing arrangements is a central goal of the crystal engineer.[1] Such control of geometry and packing, when combined with the myriad of chemical functionalities offered by a molecular approach, provides a means to design a vast array of solids with predictable and controllable properties (*e.g.* porosity, reactivity). This goal, however, is underscored by the fact that geometry and packing in the solid state are sensitive to subtle changes to molecular structure such that structurally similar molecules typically do not exhibit similar geometry and packing arrangements.[2] Thus, to confront such apparent disparity between molecular and solid-state structure, we,[3] and others,[1] are focused upon identifying geometries and packing patterns that may be used as synthons[4] to reliably control the organization of molecules in solids to achieve and control desired properties.

In this context, a property of the organic solid state that we aim to control is reactivity.[3] Specifically, we have revealed the ability of ditopic molecules, in the form of linear templates, to orient olefins in the solid state, *via* hydrogen bonds, in geometries suitable for single and multiple [2+2] photodimerizations.[2] Thus, co-crystallization of 1,3-benzenediol, or resorcinol (res), with *trans*-1,2-bis(4-pyridyl)ethylene (4,4'-bpe) produced a discrete four-component molecular assembly, 2(res)·2(4,4'-bpe),[5] held together by four O-H···N hydrogen bonds wherein two olefins were juxtaposed in a geometry suitable[2] for photoreaction. Ultraviolet (UV) irradiation of the crystalline solid produced *rctt*-tetrakis(4-pyridyl)cyclobutane in quantitative yield.[3] We have also demonstrated that the arrangement adopted by the templates and reactants is robust such that the geometry can be 'transferred' to additional solids to construct targets such as a [2.2]paracyclophane[6] and [*n*]-ladderanes (where *n* = 3 and 5).[7]

Having demonstrated the ability of res to force stacking of 4,4'-bpe in the solid state, we turn to structurally related 1,2-dihydroxybenzene, or catechol (cat). In particular, we wish to describe the formation of an infinite solid-state molecular assembly based on cat and 4,4'-bpe of composition (cat)·(4,4'-bpe).[8] Similar to resorcinol, cat can adopt more than one conformation based on the orientation of the two hydroxyl groups.[9] Specifically, two stable conformations can form: *anti-anti* and *syn-anti* (Scheme 1). In the former, the hydrogen atoms of the hydroxyl groups of the hydroxyl groups point away from each other, while in the latter one hydroxyl group participates in an intramolecular O-H···O hydrogen bond. *Ab initio* calculations indicate that the *syn-anti* conformation is more stable by approximately 5 kcal mol^{-1},[9]

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which suggested to us that cat may assemble with 4,4'-bpe in the solid state to produce, similar to 2(res)·(4,4'-bpe), a discrete hydrogen-bonded assembly that is photoactive.[10]


anti-anti   *syn-anti*
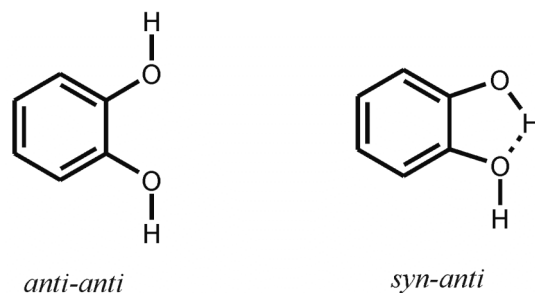
Scheme 1.

3. EXPERIMENTAL

Addition of cat (0.12 g, 1.1 mmol) to acetone (10 mL) in the presence of 4,4'-bpe (0.182 g, 1.0 mmol) yielded, upon standing for a period of approximately 2 days, yellow crystals of **1** (yield: 100%) suitable for X-ray analysis. The formulation of **1** was confirmed by ^{1}H NMR spectroscopy, as well as single-crystal X-ray diffraction.[11]

4. RESULTS AND DISCUSSION

The asymmetric unit of **1** consists of two full molecules of cat [based on O-atoms O1/O2 (cat$_A$) and O3/O4 (cat$_B$)], one full molecule of 4,4'-bpe [based on N-atoms N1/N2 (4,4'-bpe$_A$)], and two half-molecules of 4,4'-bpe [based on N-atoms N3/N3^i (4,4'-bpe$_B$) and N4/N4^{ii} (4,4'-bpe$_C$)] **(Fig. 1a)**. The components have assembled *via* O-H···N hydrogen bonds, in the sequence 4,4'-bpe$_C$···cat$_A$···4,4'-bpe$_A$···cat$_B$···4,4'-bpe$_B$ **(Fig. 1b)**, to form a one-dimensional (1D) chain based on alternating cat and 4,4'-bpe molecules.
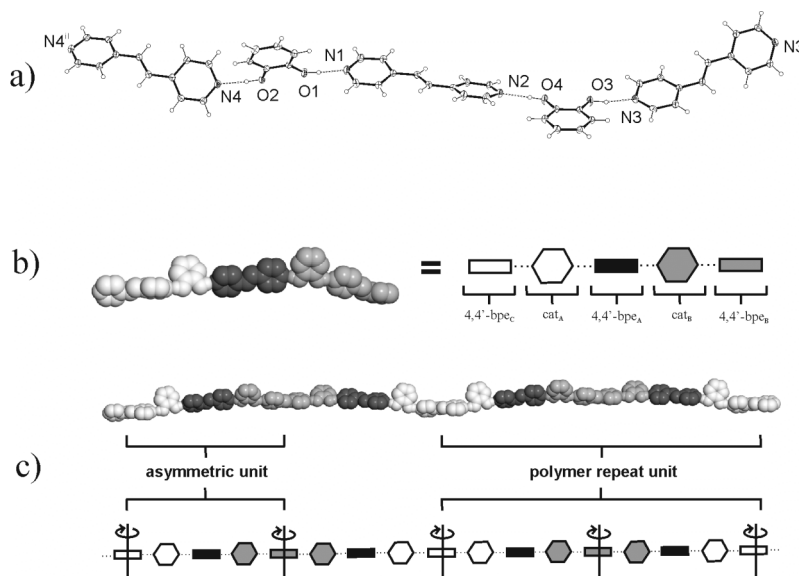
Figure 1. Perspectives of **1**: (a) ORTEP of the asymmetric unit (all non-hydrogen atoms at 30 % probability level), (b) space-filling model of the asymmetric unit along with a schematic representation, and (c) space-filling model of the eight-component repeat unit along with a schematic representation. Selected interatomic distances (Å) and angles (°): O1···N1 = 2.733(2), O1−H1O···N1 = 171.0(1), O2···N4 = 2.756(2), O2−H2O···N4 = 174.37(9); O3···N3 = 2.710(2), O3−H3O···N3 = 167.00(9); O4···N2 = 2.749(2), O4−H4O···N2 = 172.67(9). Symmetry operators: *i* = -*x*+3, *y*, -*z* + 3/2; *ii* = -*x*, *y*, -*z* + ½.

Each cat molecule adopts the *anti-anti* conformation, while the pyridyl groups of each 4,4'-bpe molecule deviate from co-planarity [pyridine···pyridine twist angles (°): 41 (4,4'-bpe$_B$); 39 (4,4'-bpe$_C$); 22.7(1) (4,4'-bpe$_A$)]. In this arrangement, the aromatic units of each hydrogen bond are either twisted or lie approximately co-planar, the twist angles involving cat$_A$ and cat$_B$ being 71° (4,4'-bpe$_A$) and 67° (4,4'-bpe$_C$), and 10° (4,4'-bpe$_A$) and 11° (4,4'-bpe$_B$), respectively. The components of the hydrogen-bonded sequence are propagated along the crystallographic [100] direction, *via* two-fold rotation axes, to give a polar, undulating chain (wavelength: 6.8 nm) based on the eight-component repeat unit 4,4'-bpe$_C$···cat$_A$···4,4'-bpe$_A$···cat$_B$···4,4'-bpe$_B$···cat$_B$···4,4'-bpe$_A$···cat$_A$ **(Figure 1c)**

The chains of **1** have self-assembled in the solid state to form centrosymmetric dimers **(Figure 2a)**. The dimers are held together by a combination of face-to-face π-π interactions, involving the pyridyl units and cat molecules, and C-H···π forces.[12] These interactions occur between peaks and troughs of adjacent polymers **(Figure 2b)**. Neighboring dimers interact *via* a combination of two-point C-H···O forces and face-to-face π-π interactions **(Figure 2c)** involving nearest-neighbor pyridyl units and cat molecules.[13] The shortest distance between neighboring carbon-carbon double bonds of **1** is 6.85 Å, involving molecules 4,4'-bpe$_A$ and 4,4'-bpe$_B$[iii] (symmetry operator *iii* = -*x*+2, -*y*+2, -*z*+1). This distance extends beyond the separation criteria of Schmidt for [2+2] photodimerization.[2] Moreover, the olefins of **1**, as determined by irradiating a powdered crystalline sample of **1** with UV-radiation (broadband Hg lamp), are photostable.

a)

b)

c)
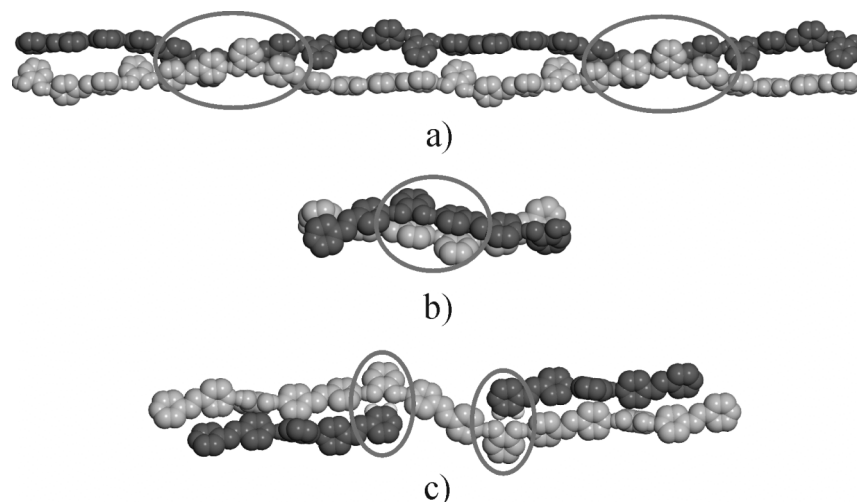
Figure 2. Space-filling views of: a) self-assembled chain dimers highlighting the peak and trough interaction, (b) interactions between the chains highlighting the π-π interactions in the central region of the fragment, and (c) interactions between the dimers highlighting the C-H···O forces (hydrogen atoms colored white).

5. CONCLUSION

In conclusion, we have revealed that cat assembles with 4,4'-bpe in the solid state to form a 1D hydrogen-bonded chain of composition (cat)·(4,4'-bpe) **1**. The cat molecules of the chain adopt the *anti-anti* conformation.[9] Efforts are currently underway to engineer cat derivatives[14] that may provide access to photoactive solids based on discrete hydrogen-bonded assemblies akin to 2(res)·2(4,4'-bpe).[15]

6. REFERENCES

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[10]   Such an assembly would involve a bifurcated interaction involving the hydroxyl group of cat that participates in the intramolecular O-H···O hydrogen bond such that cat serves as a ditopic U-shaped moiety.

[11]   Crystal data for **1**: monoclinic, *P*2/c (No. 13), $Z = 4$, $a = 23.927(2)$ Å, $b = 7.4219(7)$ Å, $c = 17.631(2)$ Å, $\beta = 109.006(5)$ °, $V = 2960.4(5)$ Å^3, 6729 unique reflections, $R = 0.0455$ [for 4512 reflections with $I \geq 2\sigma(I)$], $R = 0.0827$ (all data) and w$R^2 = 0.1627$ (all data). Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre and has been allocated with deposition number CCDC 244922.

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[13]   The *anti-anti* conformation adopted by cat in **1** may be attributed to the intermolecular forces (*i.e.* face-to-face π···π stacking, C−H···π, and C−H···O hydrogen bonds) that occur between the chains.

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