Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2017

# Hand-Twisted Helical Crystal Based Solely on Hydrogen Bonding

Subhankar Saha and Gautam R. Desiraju\*

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

E-mail: desiraju@sscu.iisc.ernet.in

## **Supporting Information**

# List of contents

- **S1:** Synthesis
- S2: Method of crystallization
- **S3:** SCXRD experiment
- S4: Crystallographic information table
- **S5:** Images of brittle crystals of **2**
- S6: Cambridge Structural Database (CSD) study
- **S7:** Computation
- **S8:** Electrostatic surface potential (ESP) map
- S9: Calculated interaction energies for model systems
- S10: Indexed faces of 3.H<sub>2</sub>O
- S11: Crystal packing in 3.H<sub>2</sub>O
- S12: Extended figure 4
- **S13:** Extended figure 5

# S1: Synthesis

# 2 (4-hydroxyphenyl 4-nitrobenzoate)

100 mg 4-nitrobenzoic acid were first refluxed with excess of thionyl chloride and 2 drops of DMF at 90°C for 3 hours in a round bottomed flask under nitrogen atmosphere. The excess SOCl<sub>2</sub> was then removed under vacuum. This produced white crude product of 4nitrobenzoyl chloride was immediately dissolved in 200 ml of anhydrous dichloromethane. This solution was then added very slowly, dropwise to a dilute solution of hydroquinone (66 mg) in 200 ml dichloromethane and a measured excess of triethylamine ( $\sim 5$  ml) for  $\sim 1.5$ hours. The resulting mixture was then refluxed for another 3 hours at 90°C with occasional stirring. Nitrogen atmosphere was maintained throughout the reaction. High dilution technique was applied to minimise the chance of electrophilic attack at both the ends of the hydroquinone. After 3 hours, the reaction mixture was cooled to room temperature and transferred to a 1 litre beaker in an ice bath, where 6N HCl solution was added slowly in order to neutralize the solution, monitoring through pH paper. The neutralized solution was subjected to solvent extraction with dichloromethane four times and finally with brine. The extracted solution was collected in a beaker containing hot anhydrous Na<sub>2</sub>SO<sub>4</sub>. A clear solution was obtained after filtration. Evaporation of solvent gave a white product which was further taken for crystallization.

# **3** (4-pyridinyl 4-nitrobenzoate)

First, 4-nitrobenzoyl chloride was prepared from 100 mg of 4-nitrobenzoic acid, following the above procedure. After that, the acid chloride was dissolved in ~ 20 ml of anhydrous THF in a 100 ml RB flask. A solution of 4-hydroxypyridine (57 mg) in anhydrous THF was then added slowly into the RB flask under continuous stirring on a magnetic stirrer. A catalytic amount of tetrabutylammonium hydrogen sulphate was added followed by a solution of  $K_2CO_3$  (~2.5 equivalent). Stirring was continued for another ~ 6 hours at room temperature. Then, the remaining THF was removed under vacuum and the mixture was extracted with EtOAc. The EtOAc solution was dried over hot anhydrous Na<sub>2</sub>SO<sub>4</sub>. A white product precipitated out after solvent evaporation and this was taken for crystallization experiments.

## S2: Method of crystallization

Compound **2** was dissolved in different aprotic solvents by sonication followed by gentle heating. The solutions were kept at room temperature for slow evaporation of the solvents. Crystals suitable for single crystal diffraction were obtained after 7 days from acetonitrile.

Compound **3** was dissolved in different aprotic solvents, like, THF, EtOAc, Me<sub>2</sub>CO and MeCN. Alcoholic solvents were avoided, as they are potential candidates for stable ester formation through degradation of the synthesized product. The solutions of **3** were kept at room temperature for slow evaporation of solvents. After ~ 10 days thin fibre like crystals were seen in a pasty kind of mixture obtained from 99% THF. This was again dissolved in

the same solvent and kept for evaporation. The process was repeated multiple times and suitable crystals for further experiments were obtained after six trials.

#### **S3: SCXRD experiment**

Single crystal X-ray diffraction (SCXRD) data of all crystals were collected on a Rigaku Mercury 375R/M CCD (XtaLAB mini) diffractometer using graphite monochromator Mo Kα radiation, with an attached low temperature gas spray cooler. The data were processed with the Rigaku CrystalClear 2.0 software.<sup>1,2</sup> Structure solution and refinements were executed using SHELX97<sup>3</sup> implemented in the WinGX suite.<sup>4</sup> All the non-hydrogen elements were refined anisotropically and hydrogen atoms were refined isotropically. The crystallographic data are given in the supplementary information, (S5).

- Rigaku Mercury375R/M CCD. Crystal Clear-SM Expert 2.0 rc14; Rigaku Corporation: Tokyo, Japan, 2009.
- [2] J. Pflugrath, Acta Crystallogr., Sect. D: Biol. Crystallogr., 1999, 55, 1718–1725.
- [3] G. M. Sheldrick, SHELX-97: Program for the Solution and Refinement of Crystal Structures, **1997** (University of Göttingen: Göttingen).
- [4] L. J. Farrugia, J. Appl. Crystallogr., 1999, 32, 837-838.

Compounds	2 3. H <sub>2</sub> O		
Formula	C <sub>13</sub> H <sub>9</sub> NO <sub>5</sub>	H <sub>9</sub> NO <sub>5</sub> C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub> .H <sub>2</sub> O	
Molecular weight	259.21	262.22	
Crystal system	Orthorhombic	Orthorhombic	
Space group	$P2_{1}2_{1}2_{1}$	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	
a (Å)	7.228(2)	3.748(8)	
<i>b</i> (Å)	7.888(3)	12.14(3)	
c (Å)	20.958(7)	26.33(6)	
α (°)	90	90	
β (°)	90	90	
γ (°)	90	90	
V (Å <sup>3</sup> )	1195.0(6)	1198(4)	
Z	4	4	
$\rho_{\rm calc}  ({\rm g/cm^3})$	1.441	1.453	
F(000)	536.0	544.0	
Temp. (K)	150	150	
$R_{I}$	0.0608	0.0985	
$wR_2$	0.1333	0.2934	
Goodness-of fit	1.056	1.166	
CCDC No.	1544054	1544055	

#### S4: Crystallographic information table

# S5: Images of brittle crystals of 2



# S6: Cambridge Structural Database (CSD) study

*Analysis of torsional angle distribution:* CSD (version 2016 with three updates) was studied for torsional angle distribution of *o*-unsubstituted phenols with 3D coordinates determined and for organic molecules.



(a) CSD (version 2016 with three updates) statistics (total number of hits= 6618) for torsional angle distribution of *o*-unsubstituted phenols (highlighted with bold lines in the schematic molecule) with 3D coordinates determined and for organic molecules. Histogram shows predominated population at lower angles only. (b, c) Schematic presentation of O–H group conformations. Former orientation can stabilize the system by extended conjugation which is absent in latter case.

*Pyridine…water interaction:* CSD was analysed for organic molecules with 3D structure determined up to vdW+0.4 Å distance.

#### **S7: Computation**

*Electrostatic surface potential (ESP) calculation:* Electrostatic surface potential (ESP) map was calculated for model compound, 4-pyridinyl acetate. The atomic positions of the model compound was fully optimized using second-order Moller–Plesset perturbation theory (MP2)<sup>5</sup> and 6-31G(d) basis set. Calculations were performed in Gaussian 09 software.<sup>6</sup> Three dimensional electrostatic surface potential was then calculated around the molecule with electron density 0.002 electron/Å. Colour coding was used to locate negatively charged (red) and positively charged (blue) surfaces.

Interaction energy calculation: Intermolecular interaction energies for N–H···O, O–H···O and C–H···O synthons were calculated using the model systems pyridine···H<sub>2</sub>O, H<sub>2</sub>O···H<sub>2</sub>O and MeNO<sub>2</sub>···H<sub>2</sub>C=CF<sub>2</sub>, respectively. MP2 method with 6-311++G(d,p) basis set was applied in Gaussian 09. The effect of Basis Set Superposition Error (BSSE) was estimated for the dimers at the optimized geometry by means of counterpoise correction (CP); as suggested by Boys and Bernardi.<sup>7</sup>

[5] C. Møller, M. S. Plesset, Phys. Rev., 1934, 46, 618-622.

[6] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09; Gaussian, Inc.: Wallingford, CT, **2009**.

[7] S. F. Boys, F. Bernardi, Mol. Phys., 1970, 19, 553-566.

S8: Electrostatic surface potential (ESP) map



ESP on N-atom in model system, 4-pyridinyl acetate.

**S9:** Calculated interaction energies for model systems with and without counterpoise correction (CP).

Model System	Interaction	Interaction energy (kJ/mol)	
		without CP	with CP
Pyridine…H <sub>2</sub> O	O–H···N	23.59	18.38
$\mathrm{H_2O}{\cdots}\mathrm{H_2O}$	0–H…0	17.83	12.33
$MeNO_2 \cdots H_2C=CF_2$	С–Н…О	4.78	3.27

# S10: Indexed faces of 3.H<sub>2</sub>O



S11: Crystal packing in 3.H<sub>2</sub>O



# S12: Extended figure 4



S13: Extended figure 5

