Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Molecular Structure 748 (2005) 57–62
Journal of MOLECULAR STRUCTURE
www.elsevier.com/locate/molstruc

Synthesis and identification of pseudopolymorphs of 4-hexyloxybenzoic acid derivative

Akhila Jayaraman, Venkataramanan Balasubramaniam, Suresh Valiyaveettil*

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore

Received 5 February 2005; accepted 1 March 2005
Available online 28 April 2005

Abstract

Compound **1** self-assembles into two crystalline pesudopolymorphic forms **1A** and **1B** with tetrahydrofuran and acetonitrile solvent molecules, respectively. In both the structures, the crystallographic aspects pertaining to the influence of solvent molecules towards facilitating the formation of hydrogen bonded networks are described. The crystal structures are stabilized through acid dimer formation, C–H···O, C–H···π and π···π interactions. The solvent molecules are stabilized in the crystal lattice through weak C–H···O and C–H···N interactions.

Keywords: Weak interactions; Solid-state self-assembly; Pseudopolymorphism; Alkoxybenzoic acid

1. Introduction

Polymormorphism and pseudopolymorphism are a common phenomena in biological systems and, therefore, understanding fundamental aspects of such phenomena has immense potential in crystal engineering studies [1]. Polymorphism is the existence of two or more different crystal structures for the same compound and pseudopolymorphism refers to the formation of one or more solvated crystalline forms of the same compound [2]. When organic compounds are crystallized from their solutions, the solvent is often eliminated from the system due to a combination of entropic and enthalpic factors. However, multipoint recognitions involving strong and weak hydrogen bonds between the solvent and the solute precludes the elimination of the solvent molecules into the bulk due to thermodynamic factors [3]. As a result, the solvent is integrated into the growing crystal. Based on CSD studies it has been shown that only 15% of the organic crystals show pseudopolymorphism and a number of such structures are reported in literature [3–6].

Hydroxybenzoic acid gave different polymorphs owing to the formation of multiple hydrogen bonds between hydroxyl and carboxylic acid groups in the lattice [7]. It can, therefore, be rationalized that the derivatives of 4-hydroxybenzoic acid such as alkoxybenzoic acids are promising building blocks for the generation of supramolecular assemblies. Alkoxybenzoic acids have been investigated for their mesomorphic properties and in the design of supramolecular liquid crystals with aza compounds [8]. 4-Hexyloxybenzoic acid undergoes four crystalline transitions before forming a nematic phase [9]. The crystal structure of 4-hexyloxybenzoic acid has been previously reported and exists in two polymorphic forms [10]. We have recently reported the existence of pseudopolymorphism in a 4-hydroxy benzoic acid derivative [11]. In this paper, we report the synthesis and X-ray crystallographic studies of a 4-hexyloxybenzoic acid derivative (**1**). Bulky biphenyl groups were incorporated to design a V-shaped (arrow) building block to promote additional stabilization through weak π–π and C–H···π interactions. Alkyl chains were introduced to explore the interplay of alkyl chain crystallization and hydrophilic interactions in the crystal lattice. Acid **1** exists as two pseudopolymorphs (**A** and **B**) which differ significantly in their crystal structures depending on the solvents used for crystallization (Fig. 1).

* Corresponding author. Tel.: +65 68744327; fax: +65 67791691.
E-mail address: chmsv@nus.edu.sg (S. Valiyaveettil).

0022-2860/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2005.03.007

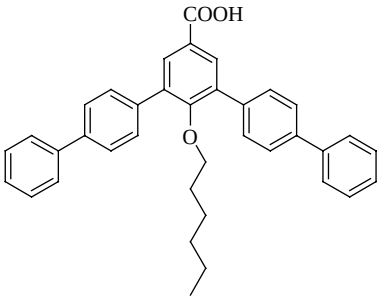


Fig. 1. Molecular structure of acid **1**.

2. Experimental section

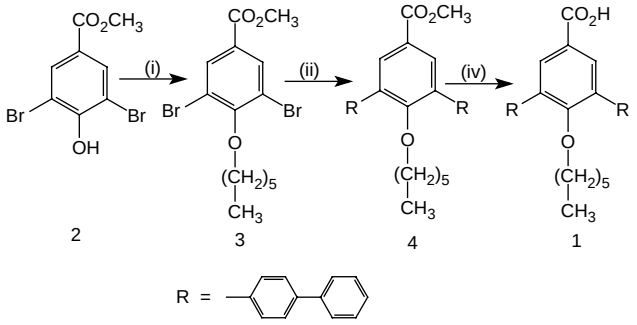
All reagents were purchased from Aldrich, Fluka, Merck and TCI and were used without further purification unless mentioned in the paper. Tetrahydrofuran (THF) was freshly distilled under N_2 over sodium. Methyl-3,5-dibromo-4-hydroxybenzoate (**2**) was purchased from Sigma Aldrich. Toluene, methyl ethyl ketone (MEK) and diethyl ether were purchased from J.T. Baker and were purified by distillation. Silica gel 60 (0.040–0.063 mm) purchased from Merck was used for column chromatography purifications. ^{1}H and ^{13}C NMR spectra were recorded using Bruker ACF 300 instrument. IR spectra were recorded using BIO-RAD FT-IR spectrophotometer. Elemental analysis was performed using Perkin Elmer CHNS Auto analyzer. Mass spectral measurements were done using Finnigan TSQ 7000 spectrometer with ESI ionization capabilities. X-ray diffraction data on single crystals were collected on a Bruker AXS SMART CCD 3-circle diffractometer with Mo K_α radiation ($\lambda = 0.71073$ Å) at 23 °C. The software used was SMART [12] for collecting frames of data, indexing reflections and determining lattice parameters; SAINT [12] for integration of intensity of reflections and scaling; SADABS [13] for absorption corrections; and SHELXTL [14] for space group determination, structure solution and least square refinements on F^2. The structures were solved by direct methods. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at fixed distances from carbon atoms.

2.1. Synthesis

The synthesis of acid **1** is given in Scheme 1.

2.1.1. Methyl hexyloxy-3,5-dibromo benzoate (*3*)

Methyl-3,5-dibromo-4-hydroxybenzoate (**2**) (10 g, 0.032 mol) was dissolved in 200 ml MEK and stirred with potassium carbonate (13.3 g, 0.096 mol) and 6-bromohexane (10.6 g, 0.064 mol). The mixture was refluxed for 24 h, filtered and concentrated at reduced pressure. The residue was extracted with ether washed with water, dried over anhydrous sodium sulphate and concentrated. The crude compound was purified by flash



Scheme 1. Synthetic route for acid **1**. Reagents and conditions: (i) $C_6H_{13}Br$, K_2CO_3, MEK, reflux, 24 h; (ii) 4-biphenyl boronic acid, 2 N Na_2CO_3, toluene, $Pd(PPh_3)_4$, reflux, 48 h; (iii) 2 N NaOH/EtOH, H^+, 8 h.

chromatography using hexane and dichloromethane as eluants to give colorless needles in 86% yield. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 0.88 (t, $J = 6.81$ Hz, 3H, CH_2), 1.01 (m,6H,-CH_2), 1.26 (m,2H,-CH_2) 3.90 (s, 3H, CH_3), 4.02 (t, $J = 6.42$ Hz, 2H, –OCH_2), 8.16 (s, 2H, Ar–H). ^{13}C NMR ($CDCl_3$, δ ppm): 13.9, 22.4, 25.3, 29.8, 31.4, 52.4, 73.8, 118.3, 127.8, 133.9, 157.3, 164.3(⟩C=O). FT-IR (KBr, cm^{-1}): 2951, 1728, 1588, 1546, 1458, 1432, 1379, 1278, 1126, 1065, 978, 762. MS-ESI: *m/z*, 391 (M^+) Elemental analysis calcd $C_{14}H_{18}Br_2O_3$ (391.96): C, 42.67; H, 4.60, Br, 40.55. Found: C, 42.86; H, 4.64; Br, 40.94.

2.1.2. Synthesis of compound (*4*)

To a vertical three necked flask equipped with a condenser was added **3** (5 g, 0.014 mol), 4-biphenyl boronic acid (7.01 g, 0.036 mol), toluene (75 ml) and 2 N potassium carbonate (75 ml). The flask was degassed three times before the catalyst, tetrakispalladium triphenylphosphine (10 mol%) was added in the absence of light under argon and contents were refluxed under inert atmosphere for 48 h. The reaction mixture was cooled, filtered, concentrated and extracted with diethyl ether. The resulting crude compound was purified using column chromatography with hexane/dichloromethane as eluent to afford **4** as a white solid in 71% yield. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 0.71 (t, $J = 7.2$ Hz, 3H), 0.97 (m, 6H), 1.21 (m, 2H), 3.35 (t, $J = 6$ Hz, 2H), 3.95 (s, 3H), 7.36 (m, 6H), 7.68 (m, 12H), 8.14 (s, 2H, Ar–H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ ppm): 13.8, 22.3, 25.2, 29.6, 31.1, 52, 73.5, 125.7, 126.7, 126.9, 127.3, 128.7, 129.7, 131.5, 135.7, 136.9, 140.1, 140.6, 158.3 (Ar-C), 166.6 (⟩C=O). FT-IR (KBr, cm^{-1}): 2955, 1727, 1554, 1441, 1373, 1282, 1115, 1007, 964, 905, 733, 598. MS-ESI: *m/z*, 540 (M^+). Elemental analysis calcd $C_{38}H_{36}O_3$ (540.27): C, 84.41; H, 6.71. Found: C, 84.03; H, 6.59.

2.1.3. Synthesis of compound (*1*)

A mixture of compound (**4**) (2 g, 0.004 mol) and sodium hydroxide (0.01 mol, 0.4 g) in ethanol–water mixture (2:1, 50 ml) was refluxed for 8 h. The solution was then acidified

with 5 N hydrochloric acid, concentrated and extracted with diethyl ether. The ether extract was washed with water and dried over sodium sulphate. The solvent was evaporated to give a white solid which was used for further characterization and crystallization, yield 96%. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 0.69 (t, 3H, J=7.2 Hz, CH_3), 0.93 (m, 6H, CH_2), 1.20 (m, 2H, -CH_2), 3.35 (t, 2H, J= 6 Hz, –OCH_2), 7.35 (m, 6H, Ar–H), 7.66 (m, 12H, Ar–H), 8.19 (s, 2H, Ar–H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ ppm): 13.8, 22.3, 25.2, 29.6, 31.1, 73.6, 124.8, 126.8, 127, 127.3, 128.7, 129.7, 132.1, 135.9, 136.7, 140.2, 140.6, 159.1 (Ar-C), 171.3(⟩C=O). FT-IR (KBr, cm^{-1}): 3028, 2930, 1686, 1595, 1485, 1422, 1377, 1338, 1267, 1227, 996, 844, 761, 729, 692. MS-ESI: *m*/*z*, 526 (M^+). Elemental analysis calcd $C_{37}H_{34}O_3$ (526.3): C, 84.38; H, 6.51. Found: C, 84.32; H, 6.54.

3. Results and discussion

3.1. Self-assembly of pseudopolymorphs *1(A–B)*

Two solvated crystals of **1** were obtained from a 1:1 mixture of tetrahydrofuran (THF)/methanol (MeOH) (**1A**) and chloroform ($CHCl_3$)/acetonitrile (CH_3CN) (**1B**) via slow evaporation method. The crystal structures of **1A** and **1B** are comparable with similar unit cell parameters and space group symmetry; however, there are differences in the nature, position and interactions of the solvent molecules in the lattice and a higher packing density for **1A**. The important crystal structure parameters and refinement data are given in Table 1.

3.2. Solid state self-assembly of *1A*

The crystal lattice of **1A** belongs to the triclinic system with a space group $P\bar{1}$. The ORTEP diagram shows the asymmetric unit containing two molecules of the acid with one molecule of disordered THF (Fig. 2a). The biphenyl rings are twisted out of plane with respect to each other. The selected torsion angles between phenyl rings are: C3–C4–C10–C11: 47(5)°; C7–C6–C22–C23: 49.1(6)°; C40–C41–C47–C48: 131.1(5)°; C44–C43–C59–C60: −139.8(4)°. The molecules are assembled into 1D chains via O–H···O hydrogen bonds from the carboxylic acid groups [O2–H2···O4: *d*(O···O): 2.65(4) Å, ∠O2–H2···O4: 178°; O5–H5···O1: *d*(O···O): 2.63(4) Å, ∠O5–H5···O1: 170° at ($x-1$, $y+1$, z) and ($x+1$, $y-1$, z), respectively]. In two dimensions, these infinite chains of molecules are stacked into staggered layers with a slight offset in a head-to-head fashion (Fig. 2b). There is no cavity in the structure and the solvent molecules establish only weak interactions with the host. The oxygen atom of the THF acts as H-bond acceptor. The interactions of the acid with the THF molecule involve C–H···O hydrogen bonds which stabilizes the lattice. The interaction parameters are C8–H8···O2S at ($1+x$, y, z): C···O: 3.15(11) Å, ∠C–H···O: 139°; C31–H31···O2S at ($1+x$, $-1+y$, z): C···O: 3.21(10) Å, ∠C–H···O: 144 °, Fig. 2c). The phenyl rings in the alternate layers are twisted with respect to each other and the distances between the layers are ca. 6 and 5 Å. The layers run parallel to each other and are stabilized via C–H···π interactions as revealed in Fig. 2d and Table 2. All C–C bonds in the alkyl chain are in *anti*-conformation except for the C35–C36 and C70–C71 bonds which have a *gauche* conformation. Alkyl chains of

Table 1
Crystal data and structure refinement parameters for pseudopolymorphs **1A** and **1B**

Form	**1A**	**1B**
Empirical formula	$C_{37}H_{34}O_3\cdot(C_4H_8O)_{0.5}$	$C_{37}H_{34}O_3\cdot(C_2H_3N)_{0.25}$
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	11.0254(1)	10.3284(1)
b (Å)	14.888(2)	14.6317(1)
c (Å)	19.0877(2)	20.7169(2)
α (°)	82.462(2)	78.213(3)
β (°)	87.878(2)	76.91(3)
γ (°)	85.493(2)	82.987(2)
Z	4	4
V (Å)^3	3095.4(5)	2975.7(5)
D_{calc} (g cm^3)	1.207	1.198
Absorption coefficient (mm^{-1})	0.076	0.075
F(000)	1200	1142
Crystal size (mm^3)	0.50×0.44×0.30	0.50×0.22×0.16
Index ranges	$-13\le h\le 13$ $-17\le k\le 17$ $-22\le l\le 22$	$-12\le h\le 12$ $-16\le k\le 17$ $-15\le l\le 24$
R(int)	0.1178	0.0514
R_1	0.0856	0.0822
wR_2	0.1786	0.2102
GOF	0.972	0.972
θ range (°)	1.64–25.00	1.43–25.00
Reflns collected	33,103	16,981
Independent reflns	10,904	10,478
Solvent	THF/methanol	$CHCl_3/CH_3CN$
Color/crystal shape	Colorless/rod	Colorless/rod

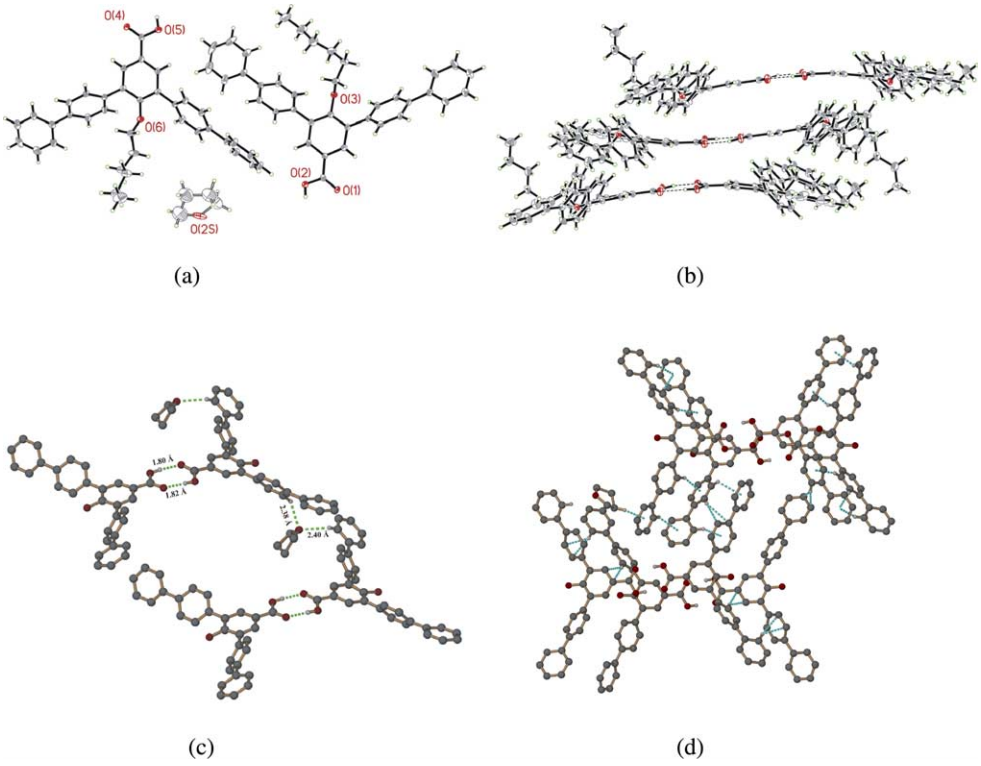


Fig. 2. (a) ORTEP diagram showing labelling scheme for form **1A** thermal ellipsoids are drawn at 30% probability level (b) 2D layer arrangement of molecules with slight offset. No interdigitation of alkyl chains was observed (c) C–H···O interactions between THF and **1**. C8–H8···O2S at $(1+x, y, z)$; C31–H31···O2S at $(1+x, -1+y, z)$ (d) interconnected C–H···π interactions shown by blue dotted lines. Symmetry operators: (x, y, z); $(x, 1+y, z)$; $(1-x, 1-y, 1-z)$; $(-x, 1-y, 1-z)$. Alkyl chains and some hydrogen atoms attached to the ring carbon atoms have been removed for clarity. Color codes: O, red; C, grey; H, green; O, red. (For interpretation of the reference to color in this legend, the reader is referred to the web version of this article.)

the neighbouring molecules in the layers do not interdigitate but pack antiparallel to each other (Fig. 2b) and are involved in C–H(alkyl)···π interactions with the phenyl rings of the adjacent molecules.

3.3. Solid state self-assembly of *1B*

The single crystal structure of form **1B** also belongs to the triclinic system with a $P\bar{1}$ space group. Each asymmetric unit consists of two molecules of **1** and a fraction of the solvent, acetonitrile. The ORTEP representation of **1B** shows two symmetry independent acid molecules (Fig. 3a). The hexyl chains in both the molecules are disordered (50/50). Similar to form **1A**, the phenyl rings are twisted out of plane with respect to each other. Each molecule of the acid is hydrogen bonded to another equivalent molecule through dimer formation by the carboxylic acid groups (O1–H1···O2 at $1-x, 1-y, -z$: O···O: 2.665(4) Å, ∠O–H···O: 170°; O4–H4···O5 at $-x, 1-y, -z$: O···O: 2.610(4) Å, ∠O–H···O: 180°). The solvent acetonitrile is weakly bonded to one of the hydrogen atoms of the alkyl chain through C–H···N interactions [C37C–H37C···N1S: *d*(H37C···N1S): 1.25 Å, ∠C37C–H37C···N1S: 127°; C37D–H37D···N1S: *d*(H37D···N1S): 0.97 Å, ∠C37D–H37D···N1S: 140°]. As seen in form **1A**, the chains of acid dimers are arranged into layers in a head to head fashion with slight offset (Fig. 3b). The alternate layers are spaced at a distance of ca. 5 Å. The molecules in the layers are stabilized by multiple C–H···π interactions (Fig. 3c). Additionally, the π···π interactions organize the phenyl rings at a distance of 4 Å and in the process stabilize the 3D network. The network is further stabilized by weak C–H···O hydrogen bond involving hydrogen atom of C59 [C59–H59···O5 at $1-x, -y, -z$: *d*(O···O): 3.418(6) Å, ∠C–H···O: 148°] (Fig. 3d). The short alkyl chains do not favour interdigitation. C33–C34 and C70A–C71A are in *gauche* conformation. All other C–C bonds in the alkyl chain are in *anti*-conformation. The C–H(alkyl)···π interactions (2.81–3.20 Å) between the aliphatic hydrogens and adjacent biphenyl rings are observed in the crystal lattice.

Table 2
X–H···C_g (π-Ring) interactions (Å, °) for **1A**

X–H···C_g	*d*(H···C_g)	*d*(X···C_g)	∠X–H···C_g
C11–H11···$C_g a^{i}$	2.91	3.579(4)	129
C19–H19···$C_g b^{i}$	2.89	3.643(6)	137
C20–H20···$C_g c^{ii}$	2.96	3.838(5)	157
C70–H70···$C_g f^{iv}$	2.90	3.661(5)	136

Symmetry codes: (i) x, y, z; (ii) $x, 1+y, z$; (iii) $1-x, 1-y, 1-z$; (iv) $-x, 1-y, 1-z$ [C_{ga}: C_{63}–C_{68}; C_{gb}: C_{57}–C_{62}; C_{gc}: C_{51}–C_{56}; C_{gd}: C_{39}–C_{44}; C_{ge}: C_{26}–C_{31}; C_{gf}: C_8–C_{13}] C_g refers to the ring centre of gravity and the alphabets represents the ring involved in interactions.

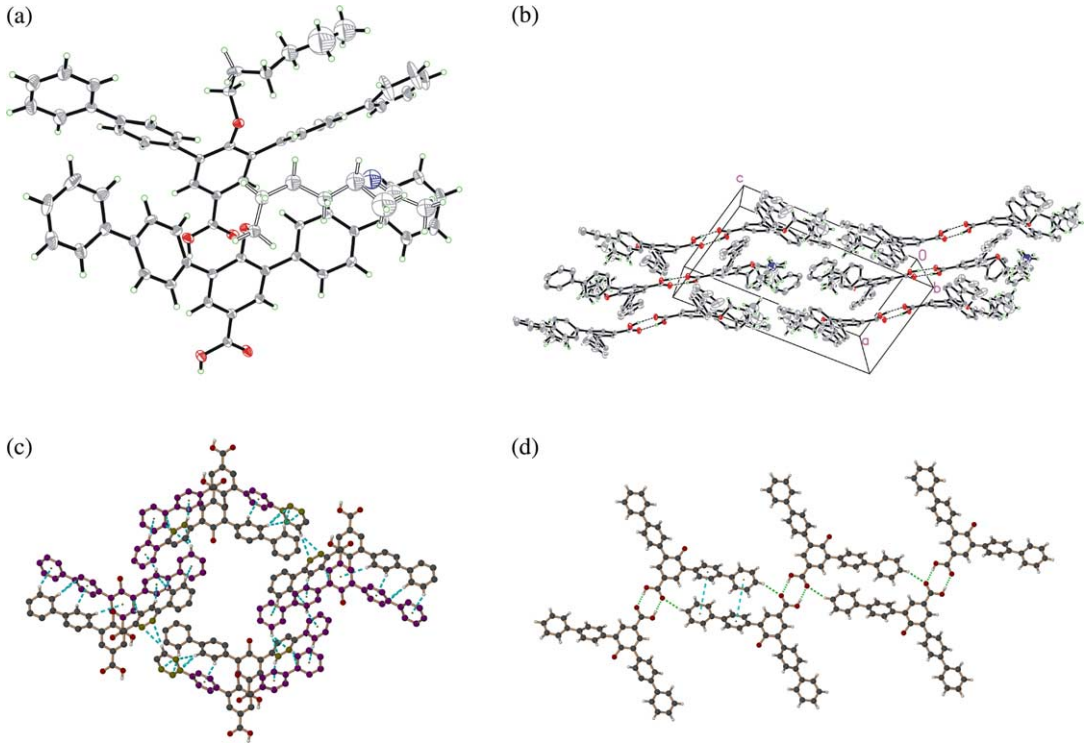


Fig. 3. (a) ORTEP diagram of form **1B** (thermal ellipsoids are drawn at 30% probability level). Color codes: C, grey; H, green; O, red; N, blue (b) 2D layer arrangement with slight offset (c) interconnected C–H···π interactions shown by blue dotted lines. The adjacent layers of the acid are shown by different colors. (d) Stabilization of the layers through C–H···O interactions, (C59–H59···O5) at $1-x, -y, -z$. Also shown is the π···π interactions between neighbouring phenyl rings, 4 Å at *x*, *y*, *z*. Alkyl chains have been removed for clarity. (For interpretation of the reference to color in this legend, the reader is referred to the web version of this article.)

4. Comparison of the pseudopolymorphs

Both **1A** and **1B** have similar packing characteristics except for the nature of the included solvent molecule. Self-recognition assisted acid dimer formation is the major hydrogen bonding motif observed in the crystal lattice. In form **1A**, the oxygen atom of THF is bonded to the acid groups through C–H···O interactions. There are two symmetry independent units in **1B** and the acetonitrile molecules are involved in C–H···N interactions with one of the hydrogen atoms of the alkyl chain. Due to the short length of the alkyl chains, no interdigitation was observed in the lattice of **1A** and **1B** and the alkyl chains from the neighbouring stacks interact laterally to pack into the available space. When **1** was cocrystallized with azacompounds such as bipyridine and pyrazine from THF solution, only **1A** was obtained. Attempts to obtain co-crystals with aza compounds in various solvents proved futile. This signifies the importance of structure regulating interactions and thermodynamic factors involved in the formation of such pseudopolymorphs [15].

5. Conclusion

Acid **1** represents a good example of pseudopolymorphic systems. The acid failed to form molecular complexes with aza compounds such as pyrazine, bipyridine and 1,10-phenanthroline but instead crystallized as solvates in the solid lattice. Acid dimer formation is the main hydrogen bonding motif inside the crystal lattice. It is expected that several other solvated forms besides the ones discussed in the paper may exist. However, repeated efforts to obtain other forms have not been successful so far. Investigations of the other possible pseudopolymorphs are currently in progress.

Acknowledgements

We thank Prof. Koh Lip Lin and Ms Tan Goek Kheng at the X-ray diffraction laboratory for their assistance in data collection and structure refinement. SV and AJ thank the National University of Singapore for funding support and research scholarship, respectively. All technical support from various laboratories at the Department of Chemistry, National University of Singapore is acknowledged.

Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2005.03.007

References

[1] H.G. Brittain, Polymorphism in Pharmaceutical Solids, Marcel Dekker, New York, 1999.

[2] (a) C. Bilton, J.A.K. Howard, N.N.L. Madhavi, A. Nangia, G.R. Desiraju, F.H. Allen, C.C. Wilson, Chem. Commun. (1999) 1675;
(b) J. Bernstein, Polymorphism in Molecular Crystals, Oxford University Press, New York, 2002.

[3] (a) Cambridge Structural Database (CSD), Version 5.15, April 1998;
(b) A. Nangia, G.R. Desiraju, Chem. Commun. (1999) 605;
(c) F.H. Allen, J.E. Davies, J.J. Galloy, O. Johnson, O. Kennard, C.F. Macrae, D.G. Watson, J. Chem. Inf. Comput. Sci. 31 (1991) 204A;
(d) V.V.S. Kumar, S.S. Kuduva, G.R. Desiraju, J. Chem. Soc., Perkin Trans. 2 (1999) 1069.

[4] (a) N. Tanifuji, K. Kobayashi, Cryst. Eng. Commun. 3 (2001) 1;
(b) R. Mondal, J.A.K. Howard, R. Banerjee, G.R. Desiraju, Chem. Commun. (2004) 644;
(c) R.K.R. Jetti, R. Boese, P.K. Thallapathy, G.R. Desiraju, J. Am. Chem. Soc. 3 (2003) 1033;
(d) R. Thanimattam, F. Xue, J.A.R.P. Sharma, T.C.W. Mak, G.R. Desiraju, J. Am. Chem. Soc. 123 (2001) 4432.

[5] (a) K. Kobayashi, A. Sato, S. Sakamoto, K. Yamaguchi, J. Am. Chem. Soc. 125 (2003) 3035;
(b) S.F. Alshahateet, R. Bishop, D.C. Craig, M.L. Scudder, A.T. Ung, Struct. Chem. 12 (2001) 251;
(c) K. Nakano, K. Sada, M. Mitya, Chem. Commun. (1996) 989;
(d) F. Toda, Y. Tagami, T.C.W. Mak, Bull. Chem. Soc. Jpn 59 (1986) 1189.

[6] (a) K. Hamada, M. Oh-hira, T. Fujisawa, F. Toda, Acta Crystallogr., Sect. C 48 (1992) 1969;
(b) V.R. Pedireddi, P.J. Reddy, Tetrahedron Lett. 44 (2003) 6679;
(c) S. Ahn, B.M. Kariuki, K.D.M. Harris, Cryst. Growth Des. 1 (2001) 107.

[7] (a) B.M. Kariuki, C.L. Bauer, K.D.M. Harris, S.J. Teat, Angew. Chem., Int. Ed. 39 (2000) 4485;
(b) E.A. Heath, P. Singh, Y. Ebisuzaki, Acta Crystallogr., Sect. C 48 (1992) 1960.

[8] (a) X. Song, J. Li, G. Liu, S. Zhang, C. Ye, E. Chen, Liq. Cryst. 29 (2002) 1533;
(b) T. Kato, M.J.F. Jean, J. Am. Chem. Soc. 111 (1989) 8533;
(c) H. Xu, N. Kang, P. Xie, R. Zhang, Mol. Cryst. Liq. Cryst. 373 (2002) 119.

[9] A. Lesac, D. Moslavac-Forjan, D.W. Bruce, V. Šunjić, Helv. Chim. Acta 82 (1999) 1707.

[10] (a) R.F. Bryan, J. Chem. Soc. (1960) 2517;
(b) R.F. Bryan, P.M. Hartley, W. Richard, Mol. Cryst. Liq. Cryst. 62 (1980) 311.

[11] J. Akhila, B. Venkataramanan, S. Valiyaveettil, Cryst. Growth Des. 4 (2004) 1403.

[12] SMART and SAINT Software Reference Manuals, Version 6.22, Bruker AXS Analytical X-ray Systems, Inc., Madison, WI, 2000.

[13] G.M. Sheldrick, SADABS, Software for Empirical Absorption Correction, University of Göttingen, Germany, 2000.

[14] SHELXTL Reference Manual, Version 5.1, Bruker AXS, Analytical X-ray Systems, Inc., Madison, WI, 1997.

[15] (a) G.R. Desiraju, Science 278 (1997) 404;
(b) V.R. Pedireddi, Cryst. Eng. Commun. 2 (2002) 315.