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Three crystalline forms of 1,3,5-benzene-tri(3-pyridinyl) carboxamide from the same solvent system

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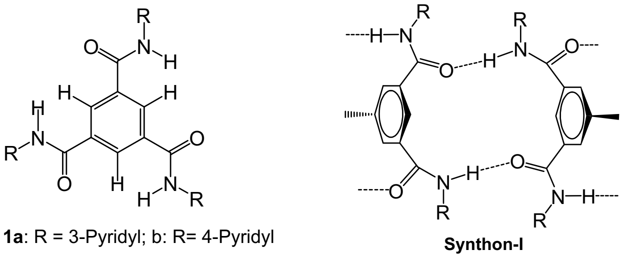
Abstract

The crystallization of the title compound from the MeOH resulted in three crystalline forms depending on the concentration of the solution, one of which contains N–H···N hydrogen bonds between pyridine and amide moieties, while the second one is constituted by amide-to-amide N–H···O hydrogen bonds and the third one crystallizes in a different crystalline phase (threads) and the phase could not be identified. These three phases have shown different behaviours in TGA and DSC studies.

Keywords: Crystal engineering; Conformations; Amides

1. Introduction

The presence of multiple functional groups in a molecule causes an interference in the formation of robust supramolecular synthons [1,2]. The interference increases with the presence of functional groups which are not self-complimentary and also with the mismatch of donor and acceptors ratios. Recently, we have reported on the interference of pyridine group in amide-to-amide hydrogen bonds by analyzing the crystal structures bis(pyridinecarboxamido)alkane derivatives [3]. In those molecules the 2°-amide groups are self complementary but not the pyridine groups as they form relatively weak C–H···N hydrogen bonded synthons. Further, in bis(pyridinecarboxamido)alkane derivatives, amide-to-amide hydrogen bonds occurred more frequently while the pyridine moieties form C–H···N hydrogen bonds with aromatic C–H groups. In continuation of our studies, we have focused on tris-amide derivatives of trimesic acid containing 3-pyridine or 4-pyridine moieties [1]. Recently the crystal structures of **1a** and **1b** have been reported and were shown that both these compounds exhibit similar supramolecular structures containing channels (Scheme 1) [4]. In contrast to the structures of bis amides, both **1a** and **1b** does not contain amide-to-amide hydrogen bonds but contain N–H···N hydrogen bonds between pyridine and amide N–H groups. To analyze these compounds further we have synthesized **1a** and crystallized in MeOH.



1a: R = 3-Pyridyl; b: R= 4-Pyridyl

Synthon-I

2. Experimental

2.1. General

FTIR spectra were recorded with an NEXUS-870 instrument, Thermo Nicolet Corporation. Elemental analyses were obtained with a Perkin-Elmer instrument, series

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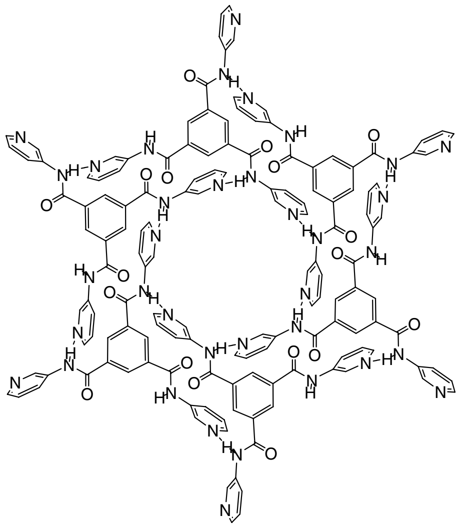

Scheme 1. Hydrogen bonding supramolecular structure observed for **1a** in A-form.

II, CHNS/O analyzer 2400. TGA and DSC data were recorded with a Perkin-Elmer instrument, Pyris Diamond TG/DTA. Powder XRD data were recorded with a XPERT-PRO PW3050/60 diffractometer.

2.2. Synthesis of *1a*

3-Amino pyridine (1.44 mmol, 1.3436 g) was added to a 40 ml of 4-picoline solution of trimesic acid (4.8 mmol, 1 g), and the solution was stirred for 15 min. Triphenyl phosphite (1.44 mmol, 4.4297 g) was added to this solution and the mixture was refluxed for 5 h. The volume of the solution was reduced to 5 ml by distilling out the picoline, and a white precipitate was obtained. The solid was filtered and washed with water and finally with acetone. Yield: 84.64%.

This product was crystallized from MeOH as described in Results and discussion and obtained the three forms. The elemental analysis of A-form is not reproducible as mentioned in the earlier report. Whereas from the elemental analysis of B-form and C-form we can conclude that both have the same composition water and they are polymorphs.

B-form (**1a**·H_2O): Calcd (%): C, 62.91; H, 4.94; N, 18.26; Obs (%): C, 63.15; H, 4.38, N, 18.42; C-form (**1a**·H_2O): Calcd (%): C, 62.91; H, 4.94; N, 18.26; Obs (%): C, 63.33; H, 4.25; N, 18.70.

2.3. Crystal structure determination

The single crystal data was collected on Bruker-Nonius Mach3 CAD4 X-ray diffractometer that uses graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) by ω-scan method. The structure was solved by direct methods and refined by least square methods on F^2 using SHELX-97 [10]. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at calculated positions and refined using a riding model.

3. Results and Discussion

Our studies show that the compound **1a** crystallizes from MeOH in three forms but not in one form as it was reported previously [4b]. One of the three is similar to the reported structure (A-form, **1a**·3MeOH), whereas as the second one (B-form, **1a**·H_2O) has an entirely different structural characteristics and exhibits synthon-**I** (Table 1). The third form (C-form, **1a**·H_2O, polymorph of B-form) we have obtained is not suitable for single crystal analysis as it was crystallized as fine threads and characterized by powder X-ray studies (Fig. 1). The CSD-analysis on the tris-amide derivatives suggests that the synthon-**I** observed here has an unique symmetry.

The process of crystallization has shown a dependency on the concentration of solution and rate of evaporation. In particular, highly concentrated solutions (5–37.5 mg/ml) found to form crystals of A-form (**1a**·3MeOH), moderate concentrations (3.5–4.2 mg/ml) were found to form B-form (**1a**·H_2O) and dilute solutions (0.5–3.5 mg/ml) are resulted in C-form (**1a**·H_2O, derived from elemental analysis). However, we found that sometimes (two times out of five trails) these concentration dependent results are not repetitive as the rate of evaporation changes with atmospheric conditions. Further, predominantly A-form was obtained from concentrated solutions if the rate of evaporation is faster. For example, if the rate of evaporation is slower, it is observed that at 20 mg/ml concentration all the three forms A, B and C, respectively, are obtained in the same crystallization flask. The source for water of crystallization could be from the washing of the product with water prior to recrystallisation from methanol or from atmospheric water. Similar results are reproduced by using anhydrous MeOH.

Table 1
Crystal data and structure refinement for B-form

Compound	B-form
Formula	$C_{24}H_{20}N_6O_4$
M. wt.	456.46
T (K)	293 (2)
System	Monoclinic
Space group	*Cc*
a (Å)	17.761 (4)
b (Å)	14.571 (3)
c (Å)	8.3610 (17)
α (°)	90
β (°)	99.87 (3)
γ (°)	90
Vol. (Å^3)	2131.8 (7)
Z	4
D_{calc} (Mg/m^3)	1.422
R_1 ($I > 2\sigma(I)$)	0.0343
wR_2 (on F^2, all data)	0.0980

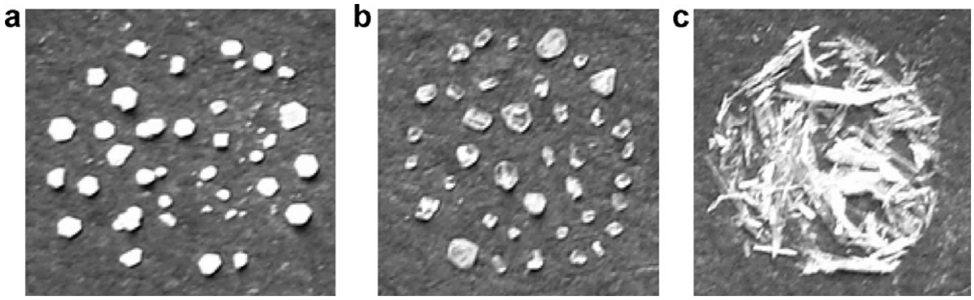

Fig. 1. Photographs of the crystals illustrating the morphological differences in three forms (a) form A became opaque as it looses the solvent; (b) form B remains perfectly crystalline at room temperature; (c) form C (thin fibers), remains crystalline at room temperature.

In A-form, the molecule maintains a 3-fold symmetry and hence it forms a honeycomb grid like structure via N–H···N hydrogen bonds. While in B-form the molecule does not exhibit a 3-fold symmetry and exhibits a T-shape geometry (Fig. 2). As a consequence they assemble via N–H···O (between amides, synthon-**I**), and O–H···N (between H_2O and pyridine) hydrogen bonds. The inter-planar angles between amide and central C_6-rings are about the same in both the forms (29.5° in A and 30°, 33.1°, 34.4 in B). However, the inter-planar angles of pyridine with central C6 (9.6°, 8.4°, 27.5°) and with amide plane in B (21.5°, 25.7°, 61.6°) are different from those in A (68°, 38.7°).

Two of the three amide groups involve in the formation of amide-to-amide hydrogen bonds with neighbouring molecules along *c*-axis such that it forms a linear chain (synthon-**I**, Fig. 3). We note here that the hydrogen bonding synthon-**I** observed in this structure does not contain an usual inversion centre but contains a glide plane (H···O, N···O, N–H···O: 2.23 Å, 3.066(2) Å, 165°; 1.96 Å, 2.787(2) Å, 162°). The third amide group of **1a** forms N–H···O hydrogen bonds with water molecule (1.98 Å, 2.770(3) Å, 152°). Two out of the three pyridine moieties involved in O–H···N hydrogen bonds with water (2.04 Å, 2.873(4) Å, 175°; 2.11 Å; 2.852(4) Å, 165°) whereas the third pyridine involved in C–H···N hydrogen bonds (2.97 Å, 3.552(4) Å, 122°). In brief, the structure can be described as a C–H···O (2.79 Å, 3.587(4) Å, 145°; 2.84 Å, 3.477(4) Å, 126°) and C–H···N (2.85 Å, 3.611(4) Å, 139°) hydrogen bonded layer structure formed by T-shaped molecules. These layers are joined together by synthon-**I** and O–H···O hydrogen bonding with water molecules (N–H···O and O–H···N). The IR spectra clearly shows the differences in carbonyl frequencies of the amide groups, which confirms the fact that carbonyls are hydrogen bonded in form B (1666 cm^{-1}) but not in form A and C (1682 cm^{-1}) [5].

The C-form has thin threads like morphology and characterized by powder X-ray diffraction. The X-ray powder analysis confirms that the diffraction pattern for C-form is different from those of form A and B (Fig. 4). Moreover, B- and C-forms are crystalline at room temperature unlike form A, which losses the solvent and there by the crystalline nature.

The three compounds have shown different melting behaviours. The form A and C shows initial melting at 186–190 °C and the remaining solid (more in case of A-form) sticks to the walls of the melting tube which finally melts at 272–274 °C (A-form) and 278–280 °C (C-form). However, B-form shows a single melting point at 272–276 °C. To study this behaviour further we have investigated TGA and DSC of these compounds (Fig. 5). In TGA, the temperatures at which they loose the solvent are different for all the three forms. A-form is loosing absorbed water [6] at 126 °C, whereas B-form and C-form loose the included water completely at about 162 and 185 °C, respectively. Therefore, up to 250 °C the weight loss is different for all there forms. However, from 250 °C

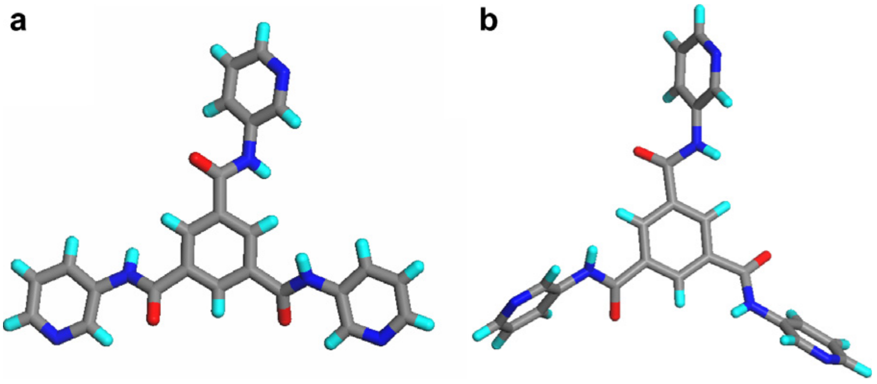

Fig. 2. Molecular structures of **1a**: (a) in the crystal structures of form B; and (b) form A; notice the difference in geometries.

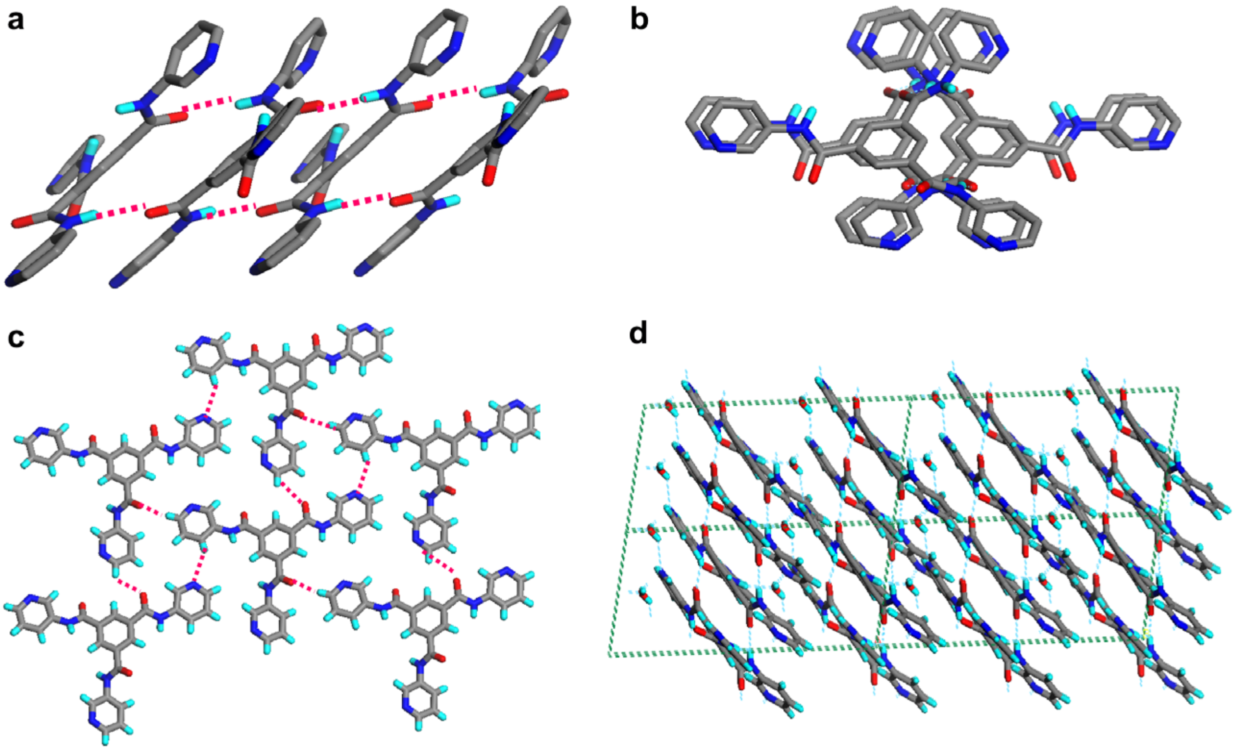

Fig. 3. Illustrations for the crystal structure of **1a** in form B: (a) 1D-chain formed via synthon-**I** along *c*-axis; (b) top view of 1D-chain; (c) 2D-layer formed via C–H$\cdots$O and C–H$\cdots$N hydrogen bonds; (d) unit cell showing the joining of the layers via hydrogen bonds, notice that the water molecules exist between the layers.

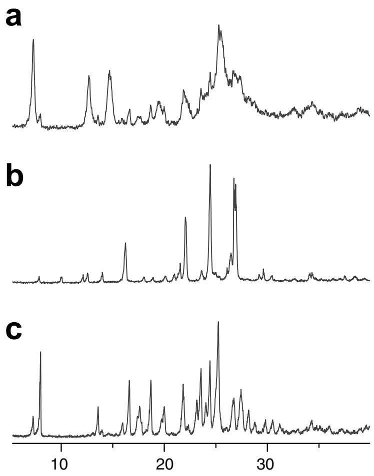

Fig. 4. Powder X-ray diffraction patterns for (a) form A; (b) form B; and (c) form C.

onwards the there forms show the similar type of thermal behaviour.

In A-form an endotherm at 95 °C and a sharp endotherm at 126 °C are observed corresponding to loss of water. Further, very small endo peaks at 196 and 226 °C were observed which may correspond to phase transitions. In B-form the mixture of exothermic and endothermic events are observed at 219, 236 and 243 °C which may correspond to the phase transitions. In form C, a sharp endotherm in the region of 204 and 212 °C indicates a phase transition. All the three forms have shown endotherms at 277–285 °C which may be the indication of decomposition of the ligand.

In order to understand the unusual symmetry observed for the synthon-**I** in B-form, we have used Cambridge Structural Database (CSD) to study the structures of compounds containing tris(amide), **1** [7]. The CSD search resulted in 14 structures containing fragment-**1** with various R-groups. Out of 14, seven structures contain non-pyridinyl groups as R-groups. In these seven structures, only three structures contain the well-known triple-helix structure (π-column) via amide-to-amide hydrogen bonds (R = $-CH_2-CH_2-OCH_3$ or $-CH(COOMe)-CH_2-CH_2-COOMe$ or $CH(COOMe)CH(CH_3)_2$) [8]. Further, none of these seven structures exhibited synthon-**I**. In the remaining seven structures, two corresponds to **1a** (form A) and **1b** [4], four contain substituted 2-pyridine groups as R-groups while one contains 2-picolyl group as R-group. Interestingly, none of these pyridine containing structures exhibit triple helix, but only one of them (R = 4-methyl-2-pyridine) exhibit synthon-**I** (Fig. 6) [9]. However, here the synthon-**I** (2.012 Å, 2.877 Å, 161.7°; 2.514 Å, 3.097 Å, 123°) has a translational symmetry unlike in B-form.

In summery, the crystallization of the compound **1a** was shown to depend on its concentration in MeOH. The lower concentrations of **1a** lead to the formation of C-form, moderate concentrations lead to B-form and highly concentrated solutions lead to crystallization of A-form. Crystal

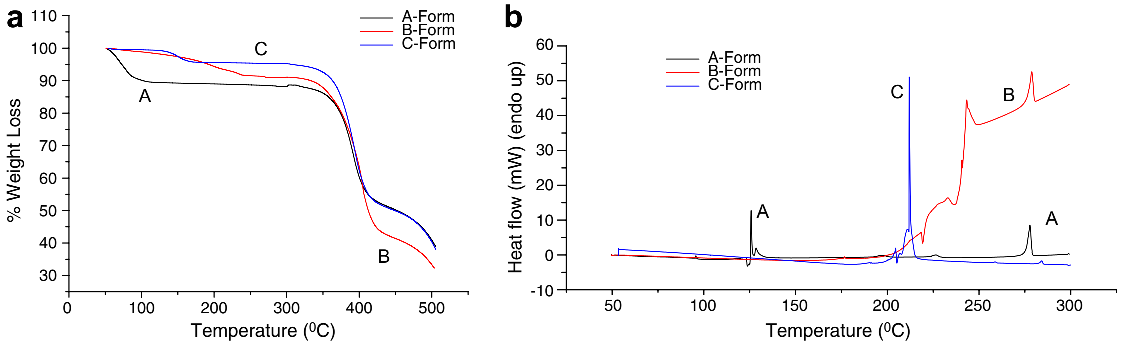

Fig. 5. (a) TGA (b) DSC spectra for the three forms.

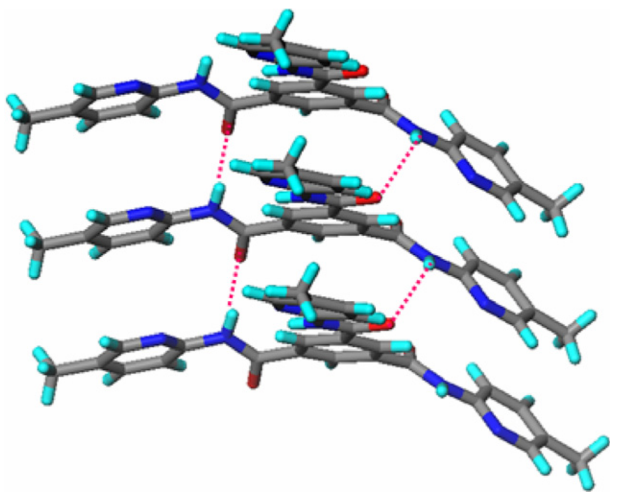

Fig. 6. Synthon-**I** with translational symmetry exhibited by 1,3,5-tris(4-methyl-2-pyridine) benzene-tricarboxamide in its crystal structure.

structure analysis confirms the fact that molecule **1a** shows conformational isomerism. Further, in A-form pyridine moiety interferes in amide-to-amide hydrogen bonds but not in form B. The CSD-analysis shows that the synthon-**I** observed here has an unique symmetry in related compounds.

Acknowledgements

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Appendix A. Supporting information

The IR spectra for three forms and crystallographic tables for B-form. CCDC 624740 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2007.07.006.

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[5] The IR-spectra for all three compounds were given in Supplementary information.

[6] This compound has been reported to take up atmospheric water after desorbtion of MeOH (Ref. [4b]). The elemental analysis after desorbtion of MeOH shows that it can take up to 5 molecules of water per one molecule of **1a**: Found: C, 54.38%; H, 5.15%; N, 15.91%; Calcd: C, 54.54%; H, 5.30%; N, 15.90%.

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