

# Solvent-Free Polymorphism Control in a Covalent Mechanochemical Reaction

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**(5)** Supporting Information

**ABSTRACT:** Four crystal modifications of a Schiff base derived from 2-hydroxy-1-naphthaldehyde and 2-aminobenzonitrile have been obtained by conventional solution-based methods. Three polymorphs out of four can be synthesized under solvent-free conditions. Herein we report simultaneous solvent-free covalent synthesis and polymorphism control of a single component system using mechanochemistry *via* neat grinding and seeding-assisted grinding, i.e. neat grinding in the presence of seed crystals. We describe the important role of seed crystals in directing the supramolecular organization of the product of covalent solvent-free reaction toward the intended polymorphic outcome. Single crystal X-ray analysis of the four crystal forms revealed conformational differences in molecules. Polymorphs display interesting and remarkably different molecular packing features *via* C-H...N and C-H...O interactions: 1D chains in form I, a 2D-network in forms III and IV, and a 3D-network in form II.

Image: spin term

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F or the design and synthesis of functional solid materials, the ability to control the solid-state assembly of molecules into crystals is of considerable importance.<sup>1</sup> In that context, extensive effort has been dedicated to the study of polymorphism:<sup>2</sup> the phenomenon of identical molecular species occupying different crystalline arrangements. The conventional approaches to controlling polymorphism, as well as the screening of different crystal forms of a compound, are still mainly based on a systematic exploration of all possible crystallization conditions, such as by varying solvent, temperature, supersaturation, etc.<sup>3</sup> An overview of currently available literature on controlling polymorphism by solvent-free methods reveals that an overwhelming majority of reported research studies have been based on melt crystallization or sublimation.<sup>4</sup> Also in that context, many studies have focused on polymorphic transformations and their control by compression, neat grinding, liquid-assisted grinding, or grinding in the presence of seed crystals.<sup>5</sup> For example, we found a report by Otsuka and Kaneniwa,<sup>6</sup> who describe that the transformation among three polymorphs of chloramphenicol palmitate in the solid state proceeds several times faster in the presence of seed crystals. Also, a recent study by Toda and co-workers<sup>7</sup> described the important role of seed crystals in the solid state inclusion complexation of 2,2'-dihydroxy-1,1'-binaphthyl. To the best of our knowledge, there is no report concerning the role of seed crystals in directing the supramolecular organization of the product of a covalent solvent-free reaction toward the intended polymorphic outcome.

Herein, we report the preparation of four crystal modifications (termed forms I, II, III, and IV) of the Schiff

base<sup>8-10</sup> derived from 2-hydroxy-1-naphthaldehyde (napht) and 2-aminobenzonitrile (abn), namely N-(2-cyanophenyl)-2hydroxy-1-naphthaldimine (1), by a conventional solvent-based method (Figure 1a).<sup>11</sup> We also report that 1 can be synthesized under solvent-free conditions<sup>12</sup> (by melting or grinding) and that the polymorphic outcome of 1 can be controlled in the solid state by different mechanochemical methods: neat grinding and seeding-assisted grinding, i.e. grinding in the presence of seed crystals. Herein, we report the relationship between all four crystal forms that was investigated by thermal analysis (DSC) and powder X-ray diffraction (PXRD) (Figure 1d). Crystals of forms I and IV, if left standing in acetonitrile vapor, convert spontaneously into form II in the period of a day. Also, grinding, i.e. kneading, of these two forms, I or IV, with a drop of acetonitrile affords once more a rapid and complete conversion again into form II. We also observed that heating of crystals of forms I or IV led to their transformation into form III (Figure 1d). Thus formed crystals of form III can be cooled to room temperature, and they are detectable by PXRD. Melting of forms II and III is observed at 192 and 197 °C, respectively (see the Supporting Information).

We were inspired to pursue the solvent-free mechanochemical experiments in our study by a recent report from Dolotko and co-workers,<sup>13</sup> who described the solvent-free synthesis<sup>14</sup> of the Schiff base derived from *o*-vanilin and *p*-toluidine. They

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Figure 1. (a) Reaction scheme of preparation of 1. Polymorphic forms of 1: (b) preparation by a conventional solution-based method; (c) twodimensional fingerprint plots; and (d) transformation conditions.

established that at room temperature solid reactants react in a liquid mixture formed upon grinding. We were also inspired by an earlier report from Jones and co-workers,<sup>15</sup> who describe "green" polymorph control of cocrystallization. They were able to control the polymorphic outcome of the mechanochemical synthesis of caffeine cocrystals by grinding solid reactants with minimal addition of a solvent of appropriate polarity. Over the past decade, mechanochemical synthesis<sup>16</sup> has shown a great potential for clean and environmentally friendly preparation of new materials.<sup>17</sup> Methods such as liquid-assisted grinding (LAG)<sup>18</sup> or ion- and liquid-assisted grinding (ILAG)<sup>19</sup> were recently demonstrated as efficient synthetic methods in both supramolecular and covalent synthesis.

We first attempted the solvent-free synthesis of 1 by manual grinding of **napht** and **abn** in the stoichiometric ratio 1:1. After 10 min of grinding at room temperature and heating up to ca. 45 °C, the reaction mixture melts and forms a liquid mixture. As revealed by PXRD and DSC, that liquid mixture, when left standing at room temperature for 20 min, yields 1. The polymorphic outcome of the product, form I, was identified by comparing its PXRD pattern with those calculated from single crystal data. Then we turned to explore the seeding of the liquid mixture with the crystals of the other forms. In the presence of a small amount of form II, the reaction resulted in the formation of form II. Equivalent attempts of seeding the melt with forms III and IV did not lead to forms III and IV, respectively. On the other hand, after neat grinding (NG) for 20 min at 20 to 25 °C, the same starting materials appear to

react without the formation of a liquid phase. As revealed by PXRD, this mechanochemical reaction also leads to the formation of 1 but this time as form II (Figure 2). However, we established that the performed mechanochemical experiment led to only partial formation of 1. A quantitative reaction of the solid reactants and pure form II was observed after 3 days standing at room temperature, based on PXRD.<sup>20</sup> Once formed, pure form II was characterized by FT-IR spectroscopy, PXRD, and DSC (see the Supporting Information). These observed results, that no liquid phase or extensive amorphous intermediate phase was identified and that the reaction proceeds upon standing of the milled mixture, can be related with a recent report from Blagden and co-workers, who describe the important role of particle size and intimate mixing of reactants in the solid state reaction.<sup>21</sup> However, water generated in the reaction can also play a significant role, since many organic reactions in the solid state proceed very efficiently and selectively in the presence of even a small amount of solvent vapor.<sup>2</sup>

Encouraged by the fact that a small amount of crystals of form II can direct the polymorphic outcome of 1 and by the fact that the reactants react in the solid state relatively slowly, we turned to grinding experiments in the presence of seed crystals. We expected that, by adding a small amount of seed crystals of a desired polymorph, we can direct the polymorphic outcome of a mechanochemical covalent synthesis toward that same form. Indeed, seeding-assisted grinding of **napht** and **abn** for 20 min at 20  $^{\circ}$ C in the presence of a small quantity of seed

# **Crystal Growth & Design**

a)

b)

Intensity



form III, solution

simulated form II

grinding

30

Form

**Figure 2.** (a) Solvent-free synthesis of the three polymorphic forms of **1**. (b) PXRD patterns of **napht**, **abn**, and polymorphs of **1** prepared by the conventional solvent-based crystallization method and by solvent-free methods and simulated patterns.

 $2\theta$  / degree

20

10

crystals of form III led to the formation of 1 as form III. As in the NG synthesis of form II, mentioned above, this experiment also led to the partial formation of 1 and the reaction of solid reactants without the formation of a liquid phase. Quantitative reaction and pure form III were observed after 8 days standing at room temperature, based on PXRD (Figure 3). The obtained pure form III was characterized by FT-IR spectroscopy, PXRD, and DSC (see the Supporting Information). Attempts to prepare forms I and IV by seeding-assisted grinding experiments have been unsuccessful. As revealed by PXRD, these experiments provided the same polymorphic outcome of 1, form II.

Single crystal X-ray analysis of the four crystal forms<sup>23</sup> of 1 revealed conformational differences in molecules. They are not planar due to the twist of the phenyl ring bonded to the amino nitrogen out of the naphthalene moiety plane. Molecules are the most planar in form I with a corresponding dihedral angle of *ca.*  $1.8^{\circ}$ , while the most nonplanar molecules are in form II with a corresponding dihedral angle of *ca.*  $35.1^{\circ}$  (Figure 4b).



Figure 3. PXRD patterns of the product of the seeding-assisted grinding experiment for a period of 8 days.



Figure 4. Polymorphic forms I-IV of 1: (a) crystals, (b) overlapped molecular structures, and (c) structural motifs.

The enol-imino tautomer was detected for all four crystal forms from the molecular geometry consideration where the C2—O1 and C11—N1 bond distances are in good agreement with analogous values of corresponding Schiff bases derived from 2-hydroxy-1-naphthaldehyde.<sup>10,24</sup> The polymorphs display interesting and remarkably different molecular packing governed by C–H…N and C–H…O interactions leading to one-dimensional chains in form I, two-dimensional networks in forms III and IV, and a three-dimensional network in form II

(Figure 4c). A comparison of the molecular geometry of 1 in all four polymorphs shows that it is significantly affected by the molecular environment and crystal packing.

In conclusion, we have obtained four crystal forms of 1 by a conventional solvent-based crystallization method. Also, compound 1 can be easily prepared by a relatively slow solid state reaction. In that context, we were able to explore the control of polymorphism in the solid state. We report the important role of seed crystals in directing the supramolecular organization of the product of the solvent-free reaction toward the intended polymorphic outcome. To the best of our knowledge, we have presented the first example of simultaneous solvent-free covalent synthesis and polymorphism control of a single component system using mechanochemistry via neat grinding and seeding-assisted grinding. The described results are important for the understanding of solid state reactivity and nucleation and can have a significant impact on the future aspects of crystal engineering and polymorphism control in the solid state. We are investigating the generality of this method, and in principle, this approach may be used to control the assembly of product molecules of other condensation reactions in the solid state.

# ASSOCIATED CONTENT

# **Supporting Information**

Experimental details for solution-based synthesis, instrumental experimental details, and PXRD, FTIR, and DSC data. This material is available free of charge via the Internet at http:// pubs.acs.org. CCDC 832329–832332 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.

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(23) Crystal data for form I:  $C_{18}H_{12}N_2O$ ,  $M_r = 272.3$ , orthorhombic,  $Pna2_1$ , a = 12.7255(11) Å, b = 26.833(2) Å, c = 3.8938(3) Å, V = 1329.58(18) Å<sup>3</sup>, Z = 4,  $D_{calc} = 1.36$  g cm<sup>-3</sup>, T = 293 K, unique refl = 1651, R = 0.065, wR = 0.097, S = 1.058. Crystal data for form II:  $C_{18}H_{12}N_2O$ ,  $M_r = 272.3$ , orthorhombic,  $P2_12_12_1$ , a = 7.6425(9) Å, b = 12.5079(11) Å, c = 13.9147(12) Å, V = 1330.1(2) Å<sup>3</sup>, Z = 4,  $D_{calc} = 1.36$  g cm<sup>-3</sup>, T = 293 K, unique refl = 1666, R = 0.034, wR = 0.087, S = 1.083. Crystal data for form III:  $C_{18}H_{12}N_2O$ ,  $M_r = 272.3$ , monoclinic,  $P2_1/n$ , a = 13.3537(4) Å, b = 7.2920(2) Å, c = 15.1552(5) Å,  $\beta = 114.823(4)^\circ$ , V = 1339.39(7) Å<sup>3</sup>, Z = 4,  $D_{calc} = 1.35$  g cm<sup>-3</sup>, T = 293 K, unique refl = 2905, R = 0.035, wR = 0.101, S = 1.089. Crystal data for form IV:  $C_{18}H_{12}N_2O$ ,  $M_r = 272.3$ , monoclinic,  $P2_1/n$ , a = 4.9647(8) Å, b = 18.738(3) Å, c = 15.175(2) Å,  $\beta = 96.223(14)^\circ$ , V = 1403.4(4) Å<sup>3</sup>, Z = 4,  $D_{calc} = 1.29$  g cm<sup>-3</sup>, T = 293 K, unique refl = 2450, R = 0.068, wR = 0.123, S = 0.958.

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