

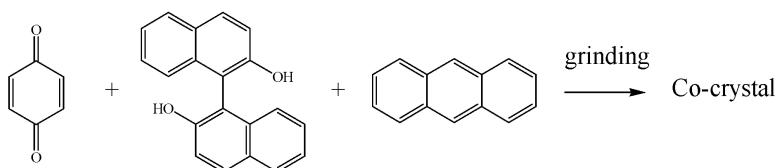
Communication

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## Direct Structure Determination of a Multicomponent Molecular Crystal Prepared by a Solid-State Grinding Procedure

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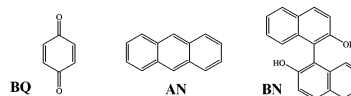
In addition to the preparation of molecular crystals by conventional solution-phase crystallization, there are a number of reports<sup>1</sup> of the preparation of molecular cocrystals by grinding together the “pure” solid phases of the constituent molecules. In many cases, single-phase cocrystals are obtained following sufficient grinding. In addition to the obvious advantages associated with solvent-free procedures for materials preparation, solid-state grinding can sometimes produce cocrystals of different structure from those obtained by cocrystallization from solution or from the melt.<sup>2</sup> For example, for the system comprising racemic bis- $\beta$ -naphthol (**BN**) and benzoquinone (**BQ**), the cocrystals obtained from solution crystallization and solid-state grinding have different structures and stoichiometries (*rac*-**BN**:**BQ** ratios of 1:1 and 2:3 respectively).<sup>1g,2,3</sup>

Clearly, solid-state grinding provides an opportunity to prepare new materials that may be difficult to obtain (and/or to isolate) by other routes and could have important implications with regard to applications based, for example, on chemical reactivity, electronic properties, and/or coloristic properties of these materials. However, to develop a fundamental understanding of the properties of such materials, an essential prerequisite is to know their structural properties. Intrinsically, materials prepared by the solid-state grinding procedure are microcrystalline powders, which are not amenable to structural characterization by single-crystal X-ray diffraction techniques. Nevertheless, recent years have seen significant advances in the opportunities for carrying out complete structure determination of molecular solids directly from powder diffraction data,<sup>4</sup> particularly through the development of the “direct-space” strategy for structure solution,<sup>5</sup> and it is clear that these techniques have a significant role to play in the structural characterization of materials prepared via the solid state grinding method. In this communication, we demonstrate the successful application of this approach in the structurally challenging case of a material containing three molecular components (Scheme 1) – *rac*-**BN**, **BQ**, and anthracene (**AN**). This material is part of a wider family of molecular cocrystals that are of interest with regard to their coloristic properties.<sup>1g,2</sup>

Grinding a physical mixture of the pure crystalline phases of *rac*-**BN**, **BQ**, and **AN** is found to produce a polycrystalline material with reddish purple color.<sup>6,7</sup> Solution-state <sup>1</sup>H NMR and elemental analysis indicate that the stoichiometry of the material is (**BQ**)<sub>1</sub>-(**BN**)<sub>1</sub>(**AN**)<sub>0.5</sub>. Crystallization from solution, on the other hand, gives a different cocrystal, with a different powder diffraction pattern (and hence different structure) and different color (bluish black).<sup>8</sup>

Powder X-ray diffraction<sup>9</sup> indicates that the solid-state grinding of *rac*-**BN**, **BQ**, and **AN** produces a new material, with no detectable

### Scheme 1



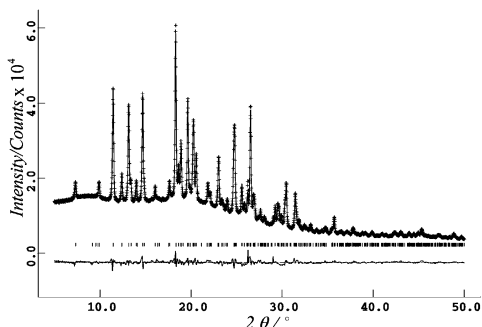
amounts of the pure phases of the individual components.<sup>6</sup> The peaks in the powder diffraction pattern are comparatively broad (a consequence of the lengthy grinding procedure), which can hinder the unequivocal determination of the unit cell parameters and space group, and standard indexing methods led to a number of unit cells with comparable figures of merit. In this situation, solid-state <sup>13</sup>C NMR played an important role in assisting the determination of the unit cell and space group. In the high-resolution solid-state <sup>13</sup>C NMR spectrum, the number of isotropic <sup>13</sup>C resonances corresponds to the number of carbon atoms in the formula unit (**BQ**)<sub>1</sub>(**BN**)<sub>1</sub>-(**AN**)<sub>0.5</sub>. From this knowledge, and assuming a standard crystal density for organic materials, the volume (*V*) of the unit cell per formula unit (*Z*) was estimated to be  $V/Z \approx 620 \text{ \AA}^3$ . From the combined evidence, a monoclinic unit cell ( $a = 27.12 \text{ \AA}$ ,  $b = 10.05 \text{ \AA}$ ,  $c = 20.32 \text{ \AA}$ ,  $\beta = 117.3^\circ$ ) with  $V = 4921 \text{ \AA}^3$  (and hence  $Z = 8$ ) obtained from indexing the powder diffraction pattern using the ITO program<sup>10</sup> was considered to be the most likely unit cell, and was indeed the unit cell with the highest figure-of-merit among the indexing solutions. Using this unit cell and systematic absences for space group *C2/c* (for which  $Z = 8$ ), a high-quality profile fitting of the complete powder diffraction pattern (using the LeBail method;  $R_{wp} = 0.0208$ ) was obtained.

Structure determination from the powder X-ray diffraction data was carried out using the genetic algorithm (GA) technique<sup>11</sup> for structure solution (implemented in the program EAGER<sup>12</sup>), followed by Rietveld refinement (using the GSAS program<sup>13</sup>). In space group *C2/c*, the half molecule of **AN** in the asymmetric unit can reside either at a center of inversion or on a two-fold rotation axis, and separate structure solution calculations<sup>14</sup> were carried out in each case. The calculation with **AN** residing on the two-fold axis yielded the trial structure with lowest *R*-factor ( $R_{wp} = 0.0649$ ) among all calculations carried out, and this structure was used as the starting model for Rietveld refinement, in which standard restraints on bond lengths and angles were used. We note that no specific restraints were imposed in “joining up” the two halves of the **AN** molecule across the two-fold axis, and despite this fact, a realistic geometry is maintained for the **AN** molecule. The good agreement between calculated and experimental powder diffraction patterns in the final Rietveld refinement<sup>15</sup> (Figure 1) vindicates the correctness of the structure.

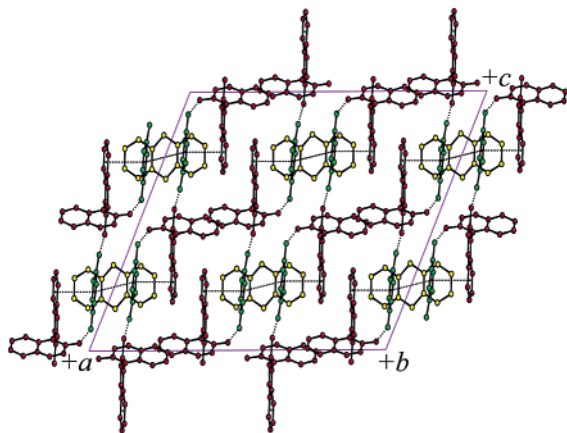
The crystal structure (Figure 2) is rationalized in terms of three different interaction motifs. First, there are edge-to-face interactions

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**Figure 1.** Experimental (+ marks), calculated (solid line), and difference (lower line) powder X-ray diffraction profiles for the three-component material after final Rietveld refinement.



**Figure 2.** Crystal structure of the three-component material (BN: red; BQ: green; AN: yellow). Dotted lines indicate the  $\pi$ -stacking interactions and hydrogen-bonded chains.

between **BQ** (edge) and **AN** (face) molecules, involving a pair of **BQ** molecules sandwiched between two parallel **AN** molecules, with the planes of the **BQ** molecules perpendicular to the planes of the **AN** molecules (which lie parallel to the  $ac$ -plane). The two **AN** molecules within a given sandwich are related by a unit cell translation along the  $b$ -axis, and this motif extends as an infinite ladder-type structure  $\cdots\text{AN}\cdots(\text{BQ})_2\cdots\text{AN}\cdots(\text{BQ})_2\cdots$  along the  $b$ -axis. Second, each **BQ** molecule in the pair discussed above engages in face-to-face interactions with a neighboring **BN** molecule, giving rise to a  $\pi$ -stacking arrangement involving four molecules ( $\text{BN}\cdots\text{BQ}\cdots\text{BQ}\cdots\text{BN}$ ) along the direction of the  $a$ -axis. A two-fold rotation axis runs perpendicular to the stacking direction and passes through the midpoint of the  $\text{BQ}\cdots\text{BQ}$  interaction. Third,  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonding involving **BN** and **BQ** molecules gives rise to chains that undulate along the direction of the  $c$ -axis. These chains involve alternating **BN** and **BQ** molecules; each  $\text{C}=\text{O}$  group of the **BQ** molecule acts as a hydrogen bond acceptor, and each  $\text{OH}$  group of the **BN** molecule acts as a hydrogen bond donor. For a given **BN** molecule, both rings are involved in hydrogen-bonding interactions, but only one ring is involved in the  $\pi$ -stacking with **BQ** molecules. Knowledge of the structural properties of this material provides a direct opportunity to understand its physical properties, most importantly its coloristic properties. Such work is now in progress.

The solid-state grinding procedure described in this report provides a route for the preparation of new materials that cannot be obtained from solution-state crystallization techniques. Such solvent-free processes for materials preparation have clear implications, inter alia, with regard to "green chemistry". Hitherto, structural characterization of materials prepared in this way has

been limited by the fact that the preparation procedure intrinsically leads to polycrystalline powders. However, as demonstrated here for the first time, new developments in techniques for determining the structures of solids directly from powder diffraction data have a key role to play in the structural characterization of new phases produced from solid-state grinding procedures, even when the peaks in the powder diffraction pattern are comparatively broad.

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**Supporting Information Available:** A table of crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (3) Unusually, it was possible in this case to determine the structures of both cocrystals from single-crystal X-ray diffraction data, as a single crystal of the phase obtained by solid-state grinding was, on one occasion, found as a very minor component during crystallization from solution.
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- (6) Grinding was carried out manually using a mortar and pestle, typically for 60 min. Depending on the relative amounts of the pure phases, the material obtained following grinding can contain residual amounts of one or more of the pure phases. Extensive trials using different relative amounts of the pure phases established the conditions for obtaining a single phase of the *rac*-**BN/BQ/AN** cocrystal. A slight excess of the pure phase of **BQ** (in comparison with the stoichiometry of the cocrystal) was necessary to produce the cocrystal as a single phase, compensating for partial sublimation of **BQ** during grinding.
- (7) The colour of the product phase (reddish purple) is markedly different from those of the pure phases of the individual components: **BQ** (yellow), **BN** (white), **AN** (white).
- (8) In contrast, for the *rac*-**BN/BQ/naphthalene** system, the same material is formed from both solution crystallization and solid-state grinding.<sup>15</sup>
- (9) Powder X-ray diffraction data were recorded at ambient temperature in transmission mode on a Siemens D5000 diffractometer [Cu  $K\alpha_1$  ( $\text{Ge-monochromated}$ ); linear position-sensitive detector covering  $8^\circ$  in  $2\theta$ ;  $2\theta$  range,  $3.5^\circ$ – $50^\circ$ ; step size,  $0.019^\circ$ ; data collection time, 10 h].
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- (14) The structure solution calculations involved one **BQ** molecule, one **BN** molecule, and half of an **AN** molecule in the asymmetric unit. The torsion angle between the two naphthol rings of the **BN** molecule was varied. There were 17 and 16 structural variables, respectively, for the calculations with the half **AN** molecule located on the two-fold axis (centroid of **AN** molecule constrained to lie on the two-fold axis) and at the center of inversion (centroid of **AN** molecule constrained to lie on the center of inversion). The calculations employed a parallel version of our GA structure solution code, with two subpopulations of trial structures allowed to evolve for 50 generations. In each generation, the two structures of lowest  $R_{wp}$  in each subpopulation were copied into the other subpopulation with 80% probability.
- (15) Final Rietveld refinement:  $a = 27.118(1) \text{ \AA}$ ,  $b = 10.0494(4) \text{ \AA}$ ,  $c = 20.3152(7) \text{ \AA}$ ;  $\beta = 117.257(3)^\circ$ ;  $V = 4921.5(3) \text{ \AA}^3$ ;  $R_{wp} = 0.0282$ ,  $R_p = 0.0209$ ; 112 refined variables, 2438 profile points.

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