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Generation of a co-crystal phase with novel coloristic properties *via* solid state grinding procedures

Reiko Kuroda,*[ab] Yoshitane Imai[b] and Nobuo Tajima[b]

[a] *Department of Life Sciences, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153-8902, Japan. E-mail: ckuroda@mail.ecc.u-tokyo.ac.jp*

[b] *Japan Science and Technology Corporation, ERATO, Kuroda Chiromorphology Project, 4-7-6 Komaba, Meguro-ku, Tokyo 153-0041, Japan*

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Co-grinding of crystals of racemic-bis-β-naphthol (*rac*-BN) and benzoquinone (BQ) produces a novel crystal adduct through crystal sheering and molecular diffusion processes in the solid state, which is structurally distinct from adducts obtained from solution or melt.

In contrast to crystallization from solution, crystallization in the solid state is rare and its mechanism has hardly been studied. We have found that co-grinding of crystals of *rac*-BN and BQ crystals, in the total absence of liquid, produces adduct crystals which are different from those obtained from solution or melt. To understand the mechanism of the adduct crystal formation, the crystallization conditions and the structures of crystals obtained from solid and solution phases have been studied.

On grinding white racemic crystals of *rac*-BN and yellow BQ in an agate mortar in a ratio of 1 : 2.5, the colour of the powder changes progressively with time from very pale yellow to pink and eventually to strong red (Fig. 1). The process was monitored by X-ray powder diffractometry. The powder diffraction pattern recorded after 20 min of grinding exhibits a new set of peaks in addition to the peaks corresponding to pure *rac*-BN and pure BQ crystals (Fig. 2a). After 45 min of grinding, the *rac*-BN and BQ peaks disappear completely and the new set of peaks becomes stronger (Fig. 2b). It should be noted that no intermediate phase is observed.

Recrystallization of the red powder crystals produced by grinding was carried out from ether/hexane (1 : 1) solution. Crystallization of a 1 : 1 mixture of BQ and *rac*-BN component crystals was also carried out from the same solvent. Both crystallization experiments produced chunky dark-red crystals (**II**) from a yellow/orange-coloured saturated solution. In a very rare case, a small amount of long thin plate-like crystals of red colour (**I**) emerged before the appearance of **II**. The structures of both **I** and **II** were determined by single crystal X-ray diffractometry.† The composition of the two crystals is different: **I** contains 1 : 1.5 *rac*-BN : BQ (*i.e.*, 1 : 1 : 3 in terms of *R*-BN: *S*-BN : BQ), whereas **II** exhibits a 1 : 1 ratio (1 : 1 : 2 in terms of *R*-BN : *S*-BN : BQ). Comparison of the observed X-ray powder diffraction pattern in Fig. 2b with that of crystal **II** (Fig. 2d) and calculated ones of **I** (Fig. 2c) and **II** (data not shown) based on the single-crystal structure unambiguously established that the red materials obtained by mixing/grinding have the same crystal structure as **I**. A measurement of the powder X-ray diffraction on **I** was not practical, as the yield of the single-crystals was very small.

The experimental results have shown clearly that simple co-grinding of crystals of component chemicals formed a new crystal. Several such cases have been reported previously by various researchers,[1] but the detailed formation process is unknown. A lubricant was used to accelerate the process in one case.[1d] Our experiments were carried out in the absence of any liquid phase. We have investigated foreseeable factors affecting the formation process. Given the low melting point of BQ (113–115 °C), it might be suggested that grinding results in a local melting of the crystals and that the adduct then crystallizes from the melt. However, grinding at low temperature did not inhibit adduct formation. Furthermore, when a mixture of BQ and *rac*-BN crystals was melted completely at *ca.* 110 °C, red material was also formed and this was shown by X-ray powder diffraction to be a new adduct crystal, **III** (Fig. 2e). We have checked by TLC that the compounds were not decomposed in the melting experiment. Together these results indicate that the grinding produced co-crystals by a mechanism that is different from crystallization from what we normally call the 'melt'.

To help understand the mechanism of adduct crystal formation by solid grinding, we have carried out various crystallization experiments, noting that **II** has a higher BN : BQ ratio than **I**. The use of higher mixing ratios than the original

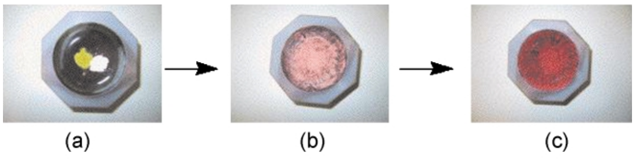

Fig. 1 Colour change of the co-ground crystals of *rac*-BN and BQ, (a) before grinding, (b) during the grinding and (c) the final product.

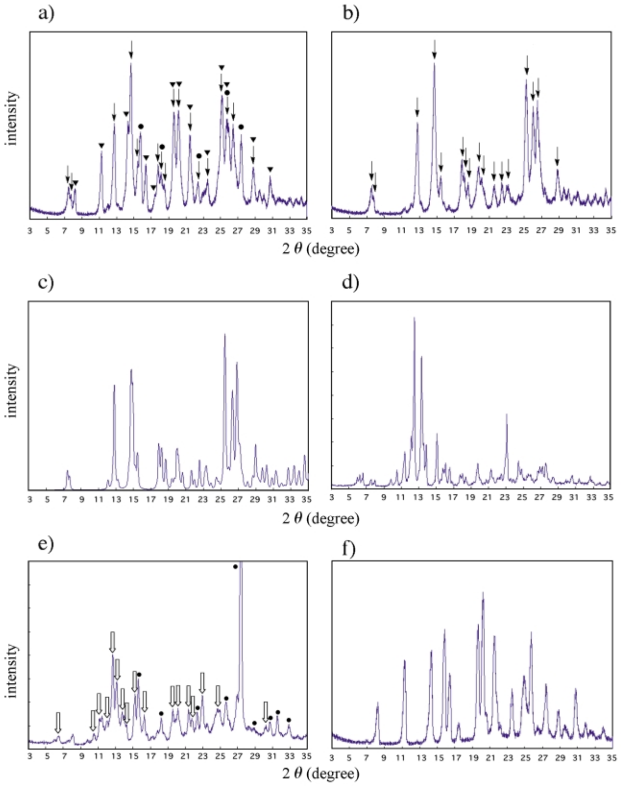

Fig. 2 X-ray powder diffraction patterns of mixtures of BQ and *rac*-BN crystals after grinding together for 20 min (a) and 45 min (b). Peaks belonging to BQ (●), BN (▼) and new crystals (↓) are indicated. (c) Calculated pattern of **I**, (d) and (e) are measured diffraction patterns of **II** and **III**. Peaks corresponding to **III** are indicated by open arrows (⇓). (f) The pattern of **I** after extended exposure to air.

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1 : 2.5 or a longer sample grinding time (as BQ easily sublimes) did not produce **II**. Co-grinding of **I** and *rac*-BN crystals did not produce **II**. Grinding **II** with BQ did not produce **I**. Grinding was carried out in the dark, under a dry Ar atmosphere, or in a metal container placed on a wet tissue in order to rule out the involvement of photons, oxygen, and static charge, respectively. None of these procedures slowed formation of the adduct. Placing *rac*-BN crystals under BQ vapour, or simply mixing crystals of *rac*-BN and BQ without grinding did not form an adduct. All these issues were judged unambiguously by colour change and X-ray powder diffraction patterns. These observations demonstrate unequivocally the necessity for direct contact between the two solids followed by mixing of the two components at the molecular level *via* appropriate sheering and diffusion processes.

The crystal structures of **I** and **II** are compared in Fig. 3. It is fortuitous that the structure of **I** was revealed, as it would otherwise require difficult determination from the powder diffraction pattern. The molecular geometries are similar in the two crystals, with only a slight difference in the central C–C torsion angles of BN (81° for crystal **I**, 75, 86 and 100° for the three independent molecules in crystal **II**).

Crystal **I**: (Fig. 3a). The asymmetric unit comprises one independent BN molecule and two independent BQ molecules, of which one resides at the centre of symmetry. A semi-column structure runs along the c axis where the aromatic planes of naphthol and BQ stack alternately. BQ is sandwiched by the naphthol rings of the *R*-BN and *S*-BN molecules, which are related by the c-glide. Only one of the carbonyl groups of BQ forms a hydrogen bond to the hydroxy group of a naphthol (O···O = 2.733 Å). The BQ on the centre of inversion forms a triplet structure sandwiched by the inversion-related *R*- and *S*-naphthol rings. Two symmetry-related hydrogen bonds are formed between the BQ carbonyl and the hydroxy group of the nearly perpendicular naphthol ring of a BN molecule (O···O = 2.703 Å).

Crystal **II**: (Fig. 3b). There are three independent molecules of BN and BQ in the asymmetric unit. The three independent BQ molecules are always sandwiched by the roughly parallel naphthol rings of two BN molecules. All possible hydrogen bonds are exploited between the carbonyl oxygen of BQ and the hydroxy group of the nearly perpendicular naphthol ring of BN molecules (O···O distance varies from 2.707 to 2.789 Å).

Theoretical calculations using the ZINDO method[2] indicated that the strong red colour of **I** and **II** which appear only in the crystal phase is due to charge transfer essentially from the 1 : 1 BN : BQ complex. The details will be reported elsewhere.

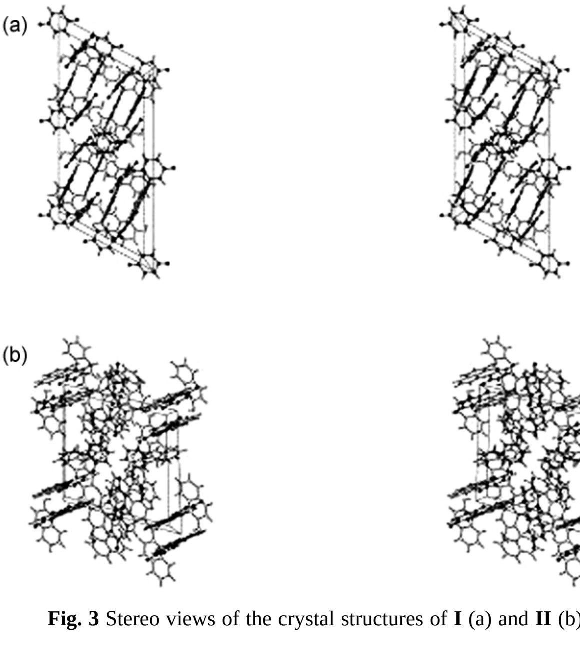

Fig. 3 Stereo views of the crystal structures of **I** (a) and **II** (b).

The local geometry of the BN···BQ···BN triplets in **I** and **II** appears similar, although the chirality is in sharp contrast. BQ is sandwiched by a racemic pair in **I**, but by a homochiral pair in **II**. In the crystal structure of pure racemic BN (space group *Iba*2), hydrogen bonds are formed between the hydroxy groups of BN molecules related by a 2_1 screw axis, thus forming a homochiral column.[1i,3] The crystal structure of pure BQ (space group $P2_1/a$) has no hydrogen bonds.[4,5] On co-grinding, BQ molecules may be inserted between the neighbouring opposite-handed homochiral BN columns of a *rac*-BN, which may encourage the formation of a hetero-chiral sandwich found in **I**. Chiral BN crystals do not form a new phase with BQ by either solid or solution crystallization. Upon complexation in the solid state, BN and BQ molecules change their crystal packing critically and form new hydrogen bonds between the two component molecules.

When adduct crystals **I** or **II** were exposed to air, the strong red colour was lost with time and, after 23 h, the crystals eventually became white. It might be expected that the crystals would deteriorate and become amorphous, but instead, they reverted to the starting *rac*-BN crystals, as unambiguously demonstrated by the X-ray powder diffraction (Fig. 2f for **I**). When the adduct crystals were placed in the vicinity of BQ crystals, no decomposition of the adducts was observed.

Crystallization by solid mixing/grinding and spontaneous crystal-to-crystal transformation both demonstrate that diffusion of molecules in the solid state can be substantial and can lead to new phases that are sometimes different from those prepared by crystallization of the same components from solution. The solid-state chemistry of these materials and the mechanisms governing their formation are clearly an exciting area for future investigation.

Notes and references

† *Crystal data*. For **I**: red crystal (0.15 × 0.33 × 0.38 mm). $C_{20}H_{14}O_2 1.5[C_6H_4O_2]$, M = 448.45, monoclinic, space group $C2/c$, a = 26.132(2), b = 13.7800(9), c = 13.9782(9) Å, β = 118.932(1)°, U = 4405.3(5) Å^3, Z = 8, D_c = 1.352 Mg m^{-3}, μ(Mo-Kα) = 0.092 mm^{-1}, 16286 measured, 5469 unique (R_{int} = 0.0308), final $R(F^2)$ = 0.046 using 3254 reflections with $I > 2\sigma(I)$, R(all data) = 0.0740. CCDC 170478. For **II**: red crystal (0.23 × 0.40 × 0.53 mm). $C_{20}H_{14}O_2[C_6H_4O_2]$, M = 394.40, triclinic, space group $P\bar{1}$, a = 14.479(2), b = 15.671(2), c = 15.725(2) Å, α = 69.792(2), β = 66.635(2), γ = 71.762(2)°, U = 3009.1(6) Å^3, Z = 6, D_c = 1.306 Mg m^{-3}, μ(Mo-Kα) = 0.088 mm^{-1}, 23185 measured, 14710 unique (R_{int} = 0.0364), final $R(F^2)$ = 0.054 using 6020 reflections with $I > 2\sigma(I)$, R(all data) = 0.140. CCDC 170479. See http://www.rsc.org/suppdata/cc/b2/b207417f/ for crystallographic files in CIF or other electronic format.

Data were collected on a Bruker APEX CCD diffractometer at 133 K and the structures were solved by the direct method using SHELX. We gratefully acknowledge Dr K. Yoza and Mr S. Igarashi of Bruker Japan for the crystallographic data collection.

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