Spontaneous rearrangement of hydrogen bonding in a crystalline state

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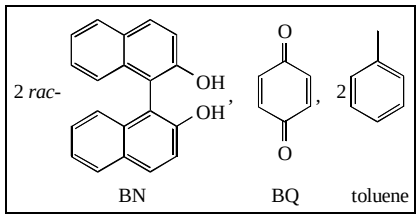
10.1070/MC2003v013n03ABEH001805

Spontaneous rearrangement of hydrogen bonding in a crystalline phase was observed in molecular crystals, which included sublimable benzoquinones.

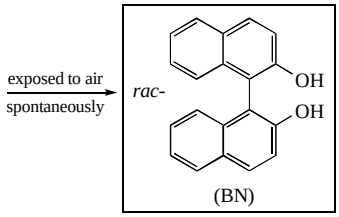
Chirality is a fundamental aspect of nature and is expressed at all levels, either microscopic or macroscopic, and either animate or inanimate. It is particularly important in life as the biological world is homochiral. We have been studying molecular recognition,[1] chirospectroscopy[2] and supramolecular chirogenesis[3] in a crystalline state, where chiral discrimination energy is orders of magnitudes larger as compared with a solution state. In many cases, hydrogen bonding plays a key role in determining whether a chiral or racemic crystal will form. For example, structures of the historically famous Pasteur's chiral and Scacchi's racemic sodium ammonium tartrate crystals that we have determined[4] contain different numbers of water of crystallization and substantial hydrogen bonding among tartrate ions, water of crystallization and ammonium ions. Hydroxyl hydrogen atoms of a tartrate ion adopt different orientations in the chiral and racemic crystals in order to form two intramolecular hydrogen bonds in the chiral crystal but one intra- and one intermolecular hydrogen bonding in the racemic crystal.[4] Here we report an interesting case where this important hydrogen bonding is spontaneously rearranged in a solid state.

Previously, we reported[5] the formation of black three-component inclusion crystals (crystal **I**) with a 2:1:2 stoichiometry of *rac*-BN: BQ: toluene, where *rac*-BN = racemic bis-β-naphthol and BQ = benzoquinone. In a crystal of **I**, which has the space group $P\bar{1}$ (#2), there is substantial hydrogen bonding involving hydroxyl groups, as in the case of sodium ammonium tartrate. *R*-BN, BQ and *S*-BN form a triplet structure, where BQ is sandwiched in parallel with one of the two naphthyl ring planes of *R*-BN and *S*-BN, along the crystal axis *c*. The π–π stacking gives rise to the black colour. The two carbonyl oxygen atoms of BQ each form two hydrogen bonds with the OH of the non-parallel naphthyl ring of *R*- and *S*-BN within the triplet. An additional hydrogen bond is formed between the carbonyl oxygen of BQ and the OH of a near-parallel naphthyl ring, which belongs to the neighbouring triplet. In this manner, a continuous hydrogen-bonded column along the crystal axis *a* is formed. Two toluene molecules, which are related by an inversion centre, are included in a continuous channel-like cavity along the axis *c* and fixed in place by two weak C–H···π interactions per molecule (see Figures 1 and 2 in ref. 5).

When the black crystals are exposed to air, the crystal colour changes from black to white within one day (in the case of microcrystallites) or a few days (single crystals). The colour change was monitored by X-ray powder diffractometry (Figure 1). Samples were softly ground, and 20 mg of samples were mounted on a sample plate. Diffraction data were recorded on a Rigaku Multi Flex X-ray diffractometer with graphite-monochromated CuKα_1 radiation (λ = 1.5418 Å), repeatedly after an appropriate time of exposure of the sample to air. The scan was made in the range $3° \leq 2\theta \geq 35°$ in 0.02° steps and recorded over a total of 11 min. It might be expected that the crystals would deteriorate to become amorphous; however, as is seen in Figure 1, the peaks corresponding to the black inclusion crystals (black arrows) decreased in intensity, while new peaks (white arrows) appeared [Figure 1(*b*) and (*c*)]. Eventually, the peaks corresponding to the black crystals disappeared completely [Figure 1(*d*)]. Surprisingly, the final powder diffraction pattern is identical to that of crystalline *rac*-BN. No intermediate peaks are observed (Scheme 1).



Crystal **I**



Crystal of *rac*-BN

Scheme 1

rac-BN crystallises in the space group *Iba*2; hydrogen bonds are formed between the hydroxyl groups of 2_1-screw related BN molecules, thus forming a homochiral column along the axis *c*.[6,7] During the process of toluene and BQ loss, hydrogen bonds between BN and BQ are severed and BN molecules spontaneously rearrange themselves to form new hydrogen bonds among themselves. When the crystals are kept under both toluene and BQ vapour, they retain the black colour. Intermediate diffraction patterns are compared for the two cases where a crystal of **I** is placed under only toluene vapour or only BQ vapour. When placed under BQ vapour, the crystals rapidly decomposed, as is expected from their channel-like cavity structure. Interestingly, three peaks at 2θ = 9.2, 13.1 and 18.3° disappeared rather quickly and the peaks around 2θ = 12.5~13.8° remained for a long time. The order is opposite under an atmosphere of toluene; peaks around 2θ = 12.5~13.8° disappeared quickly, whereas the three peaks (2θ = 9.2, 13.1 and 18.3°) disappeared more slowly. Finally, the crystals turned to *rac*-BN in both cases. This may give some clue as to the mechanism of hydrogen bond rearrangement.

This interesting spontaneous rearrangement of a hydrogen bond network initiated by the loss of volatile compounds from crystals was first reported for the two-component inclusion crystals consisting of 1:1.5 *rac*-BN: BQ (Crystal **II**) or 1:1 *rac*-BN: BQ (Crystal **III**).[8] When crystals **II** or **III** were exposed to air, they lost their strong red colour and became white after a while. We monitored the colour change of **II** by X-ray diffraction as shown in Figure 1. The X-ray powder diffraction unambiguously demonstrated that these two-component crystals also reverted to the starting *rac*-BN crystals without going through an intermediate amorphous phase.

These results suggest that the diffusion of molecules in a solid state can be considerable, and hydroxyl groups can easily change hydrogen-bonding partners in solid systems, where volatile or sublimable compounds are involved. The detailed mechanism of the diffusion process and hydrogen bond rearrangement is currently being studied.

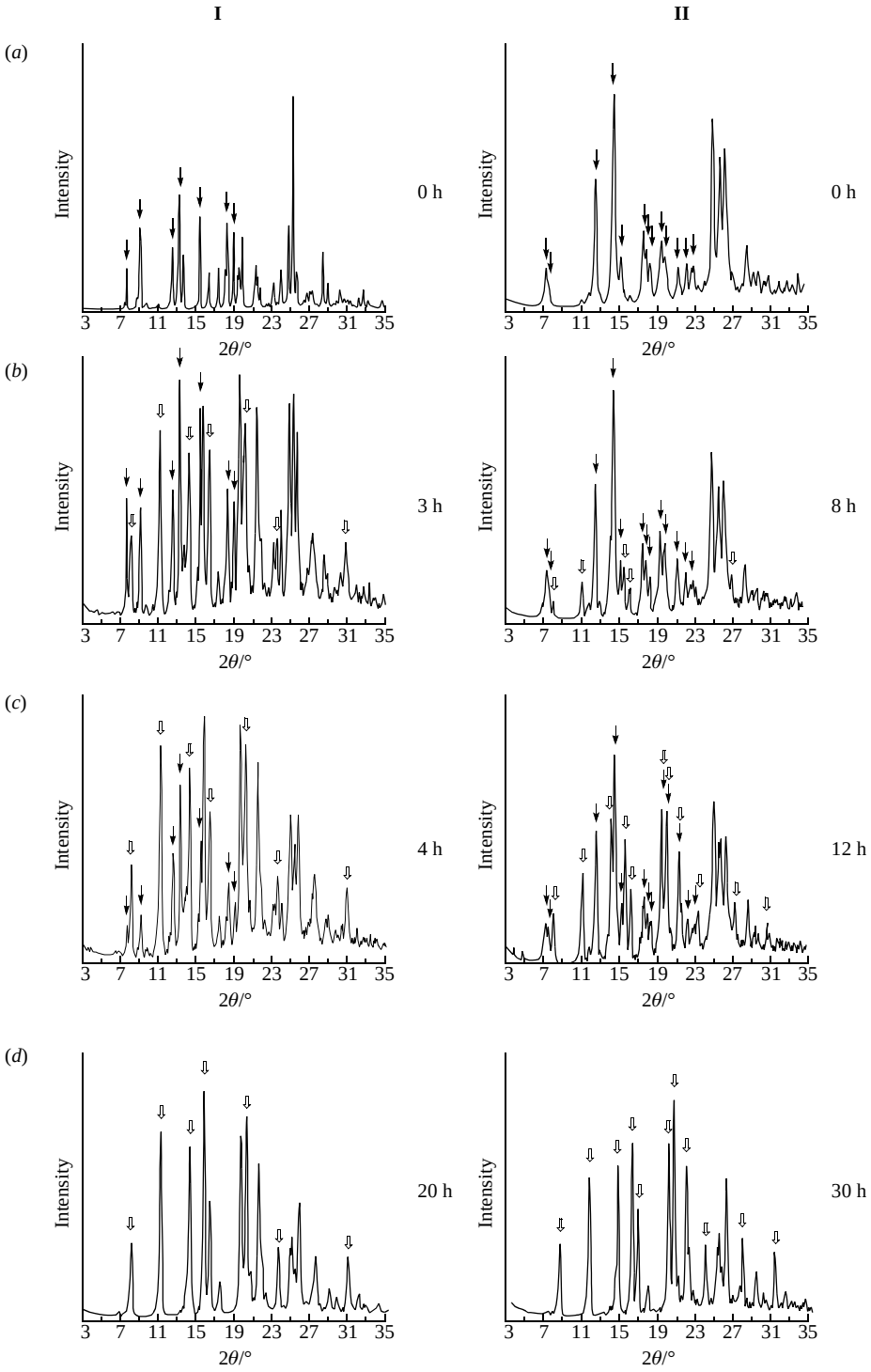


Figure 1 Time-course X-ray powder diffraction patterns of crystals **I** and **II** during the colour change at the initial (*a*), intermediate (*b*) and (*c*) and the final (*d*) stages.

References

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Received: 23rd May 2003; Com. 03/2131