Temperature-controlled selectivity of isomeric guest inclusion: enclathration and release of xylenes by 1,1′-binaphthyl-2,2′-dicarboxylic acid

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Selectivity of enclathration and desolvation of xylene isomers by a dicarboxylic host depends on temperature.

Selective inclusion of guest species during crystallization is becoming of increasing importance in both the chemical and pharmaceutical industries, thus giving rise to the study of this phenomenon.[1,2] Recently, 1,1′-binaphthyl-2,2′-dicarboxylic acid (BNDA) was reported as a new clathrate host, and was found to exhibit clathrate formation selectivity for guests containing hydroxy groups.[3] However, a dependence of this selectivity upon the thermodynamic conditions of crystallization, such as that described here for the inclusion of xylene isomers, has not been discussed before.

Crystallization of BNDA from xylene isomers at room temperature gives three different channel-type clathrates.† In these crystals the BNDA molecules are incorporated into infinite zigzag chains created by H-bonded carboxylic group dimers. In the BNDA/*m*-xylene clathrate [Fig. 1(*a*)] these chains run along the *c*-axis and stack parallel to the *ac* plane in a ‘face-to-face’ mode, while in the BNDA/*p*-xylene clathrate [Fig. 1(*b*)] the chains are displaced by 1.5 Å along the *c*-axis. There are two BNDA molecules in the asymmetric part of the unit cell of the BNDA/*o*-xylene clathrate [Fig. 1(*c*)] which form zigzag chains in the [011] direction. Owing to the packing of these chains, two different channels are formed in the crystal.

In addition, simultaneous differential scanning calorimetric (DSC) and thermogravimetric (TG)‡ investigations of the thermal decomposition of these clathrates have been performed (Fig. 2). The release of the guest molecules during a linear temperature scan occurs in the temperature intervals 50–100 °C and 100–120 °C for the BNDA clathrates of *o*- and *p*-xylene, respectively. The observed mass losses correspond to the results of the X-ray structure analysis. Heats of clathrate decomposition have been calculated from the DSC curves to be 58 ± 1 and 49 ± 2 kJ mol^{-1} for the *p*- and *o*-xylene clathrates, respectively. These values are considerably higher than the heat of evaporation of xylenes (36 kJ mol^{-1}), suggesting specific stabilizing interactions in the clathrate crystals. The *m*-xylene clathrate of BNDA, however, causes problems in the TG-DSC because of its high instability; during sample preparation for an experiment the crystals lost *ca*. 30% of the included *m*-xylene molecules. Therefore, the determined host–guest ratio does not exactly correspond to the X-ray data. Nevertheless, based on the mass loss during the TG-DSC experiment a heat of decomposition of *ca*. 30 ± 5 kJ mol^{-1} has been estimated. The lower precision is caused by the uncertainty of the DSC baseline due to the sample instability. Taking into account this limited accuracy the heat of decomposition of the BNDA/*m*-xylene clathrate is much lower than the values determined for the stable BNDA clathrates and compares to the heat of evaporation of xylene.

The decomposed products obtained by vacuum desolvation (0.5 mbar, 8 h) of the BNDA clathrates at different temperatures were also characterized by X-ray powder diffraction.§ The BNDA clathrates with *m*- and *o*-xylene can be decomposed to

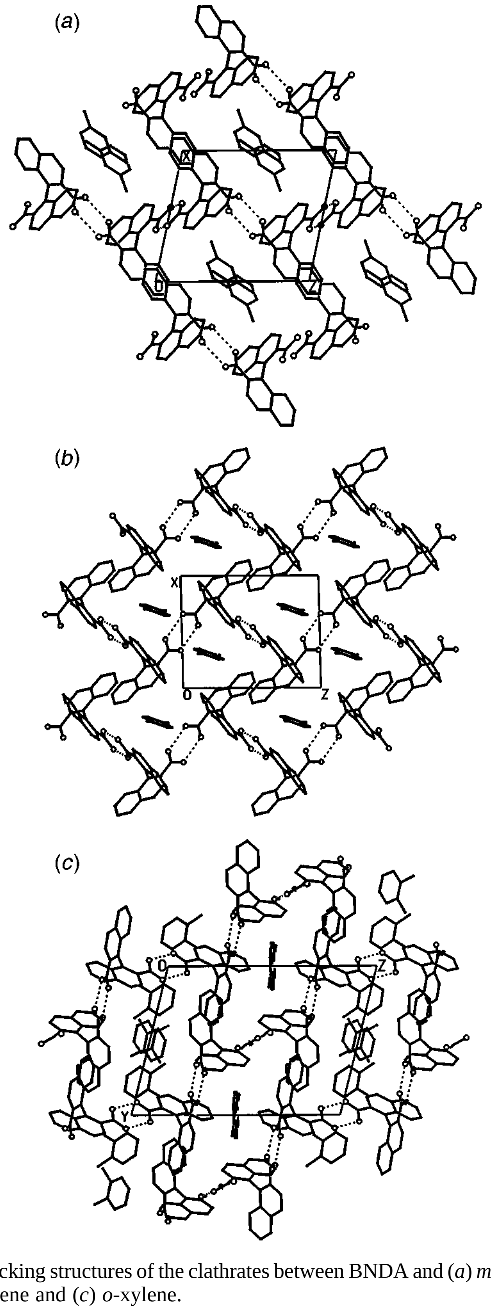

Fig. **1** Packing structures of the clathrates between BNDA and (*a*) *m*-xylene, (*b*) *p*-xylene and (*c*) *o*-xylene.

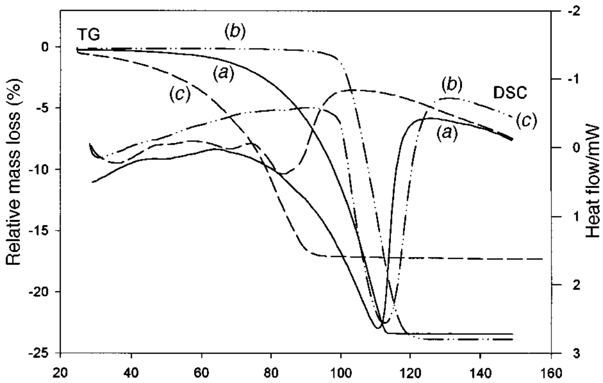

Fig. 2 Thermal degradations of (*a*) BNDA/*o*-xylene, (*b*) BNDA/*p*-xylene and (*c*) BNDA/m-xylene clathrates.

yield a desolvated phase **P1** of BNDA at 50 °C while the desolvation of the BNDA/*p*-xylene clathrate at higher temperature (100 °C) gives only a guest free phase **P2**. Recently, a crystal structure of the orthorhombic phase **P2** has been reported,[4] whereas single crystals of the triclinic phase **P1** have only now been obtained at 80 °C from an equimolar mixture of xylene isomers and its crystal structure has been determined.† The measured diffraction patterns of the desolvated samples correspond to theoretical diffractograms calculated from the appropriate structure data.

The different stabilities of the BNDA/xylene clathrates outlined above suggest a probable enclathration selectivity for the different xylene isomers, which prompted us to study the formation of BNDA clathrates from an equimolar mixture of the three xylene isomers. X-Ray diffraction and TG-DSC techniques were used to identify the obtained crystals. The crystallization temperature was varied within over −10 to +80 °C. If the crystallization temperature is between −10 and +10 °C a stable BNDA/*p*-xylene clathrate was found. Around room temperature a mixture of crystals of BNDA/*p*- and *o*-xylene clathrates was formed. TG-DSC curves of this crystal mixture are presented in Fig. 3 showing the two phases as distinctive steps. At +40 and +60 °C crystals of the BNDA/*o*-xylene clathrate were obtained, and crystals of the triclinic phase **P1** were formed at +80 °C. However, crystallization of the *m*-xylene clathrate from the mixed solution did not occur.

Thus, formation of clathrates or guest free host compounds and enclathration selectivity for a given host may be controlled by varying the crystallization temperature. These findings can be applied to purification and separation problems of isomeric mixtures or for the preparation of compounds of interest in different crystal forms having different stability, composition, solubility *etc.*

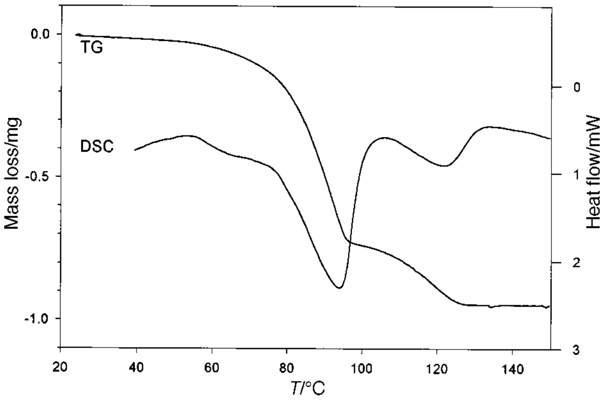

Fig. 3 Thermal degradation of the mixture of BNDA/*o*- and *p*-xylene crystals obtained at room temperature from a solution of an equimolar mixture of the three xylene isomers.

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Notes and references

† *Crystal data*: intensity data were collected at room temperature on a Syntex $P2_1$ diffractometer using Cu-Kα radiation (λ = 1.54178 Å) for the BNDA/*m*-xylene crystal and on an Enraf-Nonius CAD-4 diffractometer using Mo-Kα radiation (λ = 0.71073 Å) for the other three crystals.

BNDA/*o*-xylene: $C_{60}H_{48}O_8$, M = 896.98, triclinic, $P\bar{1}$, a = 10.843(2), b = 12.954(3), c = 17.599(4) Å, α = 103.64(3), β = 94.69(3), γ = 92.39(2)°, V = 2389.4(9) Å^3, Z = 2, D_c = 1.180 g cm^{-3}, μ(Mo-Kα) = 0.080 mm^{-1}, F(000) = 892, crystal size 0.2 × 0.35 × 0.45 mm, 10244 independent reflections. Final R = 0.0876 for 4648 reflections with $I > 2\sigma(I)$ and $wR2$ = 0.3288 for all data.

BNDA/*m*-xylene: $C_{30}H_{24}O_4$, M = 448.49, triclinic, $P\bar{1}$, a = 10.117(2), b = 10.556(2), c = 11.864(3) Å, α = 77.19(3), β = 77.81(3), γ = 86.63(2)°, V = 1207.5(5) Å^3, Z = 2, D_c = 1.233 g cm^{-3}, μ(Cu-Kα) = 0.651 mm^{-1}, F(000) = 472, crystal size 0.2 × 0.4 × 0.5 mm, 3400 independent reflections. Final R = 0.0544 for 2470 reflections with $I > 2\sigma(I)$ and $wR2$ = 0.1477 for all data.

BNDA/*p*-xylene: $C_{30}H_{24}O_4$, M = 448.49, triclinic, $P\bar{1}$, a = 10.117(2), b = 10.520(1), c = 11.913(1) Å, α = 83.48(1), β = 89.27(1), γ = 72.64(2)°, V = 1202.0(3) Å^3, Z = 2, D_c = 1.239 g cm^{-3}, μ(Mo-Kα) = 0.082 mm^{-1}, F(000) = 472, crystal size 0.35 × 0.5 × 0.5 mm, 5228 independent reflections. Final R = 0.0486 for 3938 reflections with $I > 2\sigma(I)$ and $wR2$ = 0.1493 for all data.

Polymorph **P1** of BNDA: $C_{44}H_{28}O_8$, M = 684.66, triclinic, $P\bar{1}$, a = 9.932(2), b = 11.320(2), c = 15.733(3) Å, α = 81.75(3), β = 80.57(3), γ = 89.34(3)°, V = 1726.8(6) Å^3, Z = 2, D_c = 1.317 g cm^{-3}, μ(Mo-Kα) = 0.091 mm^{-1}, F(000) = 712, crystal size 0.1 × 0.3 × 0.5 mm, 7529 independent reflections. Final R = 0.0624 for 3528 reflections with $I > 2\sigma(I)$ and $wR2$ = 0.2227 for all data.

The structures were solved by direct methods using the program SHELXS-86. The refinement of the structures against all $|F^2|$ data was carried out by the program SHELXL-93 with anisotropic displacement parameters for non-hydrogen atoms, and isotropic parameters for the guest molecules in the BNDA/*o*-xylene complex and the disordered O atoms in the polymorph **P1**. The H-atoms of all structures were placed at the calculated positions. CCDC 182/1100.

‡ *Thermal analysis*: The thermal decomposition of the different clathrate phases was studied by means of a simultaneous TG-DSC 111 system (Seteram, France) using open aluminium crucibles, sample weights of *ca.* 4 mg, a linear heating rate of 5 K min^{-1} and argon at 1 l h^{-1} as purge gas for all measurements. Crystals of an average size of 0.5–1 mm were taken from the mother liquor, quickly dried on filter paper and transferred into the crucible for immediate weighing and performance of the TG-DSC experiments

§ *X-Ray powder diffaction analysis*: Experiments were performed using a horizontal goniometer HZG 4 (Präzisionsmechanik Freiberg, Germany) and Cu-Kα radiation.

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