Mechanochemical preparation of adducts (co-crystals and molecular salts) of 1,4-diazabicyclo-[2.2.2]-octane with aromatic polycarboxylic acids†

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Solid-state adducts (co-crystals and molecular salts) of 1,4-diazabicyclo-[2.2.2]-octane (DABCO) with aromatic polycarboxylic acids (isophthalic acid, $isoH_2$, dinicotinic acid, $dinH_2$ and dipicolinic acid, $dipH_2$) were prepared in the solid state by grinding and kneading techniques, and fully characterized *via* X-ray diffraction. The polycarboxylic acids differ for the presence/absence and position of a nitrogen atom in the aromatic ring; the extent of proton transfer, from the carboxylic groups on the acids to the nitrogen atoms on DABCO, reflects the trend of solution acidity of the three polycarboxylic acids.

Introduction

Mechanochemistry is an attractive and ecofriendly alternative route to the synthesis of crystalline materials by grinding together solid reactants.[1] With the crystal engineering field booming,[2] the mechanical mixing of crystalline solid reactants has become the method of choice to obtain co-crystals,[3] salts[4] and coordination complexes and networks.[5] Mechanical mixing of solid reactants not only allows preparation of new crystal forms, often not accessible from solution, but also represents a green way for the preparation of new materials, because the solvent is either absent or used in catalytic amount.

Over the past decade we have actively investigated the utilization of these methods in crystal engineering for the preparation of supramolecular aggregates, co-crystals and coordination complexes.[5]

We have reported, *inter alia*, the mechanochemical preparation of hydrogen bonded adducts of 1,4-diazabicyclo-[2.2.2]-octane, DABCO, with a series of dicarboxylic acids of increasing aliphatic chain length, $HOOC(CH_2)_nCOOH$ ($n = 1–7$).[5]

In this communication we report the results of an extension of this study to the preparation, both by solution and mechanochemical methods, of co-crystals of DABCO with aromatic polycarboxylic acids (see Chart 1).‡

Aza-donor molecules are important building blocks in crystal engineering because of their ability to coordinate to metal centres and forming robust hydrogen bonded networks; several studies have been carried out by many research groups to show the ability of aza-donor molecules in the formation of a variety of co-crystals, salts and solvates with aromatic and aliphatic carboxylic acids *via* the formation of strong and directional O–H⋯N hydrogen bonds.[6] DABCO, on the other hand, is a ternary amine with a strong tendency to form a variety of co-crystals with acids, phenols, and amines.[7] It is also used as a structure-directing

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‡ All reagents were purchased from Sigma–Aldrich and were used without further purification.
Solid-state synthesis. In the solid-state reactions DABCO and isophthalic, dinicotinic or dipicolinic acid were manually ground together in an agate mortar in 1 : 1 molar ratio for *ca.* 20 min. In all the kneading experiments a few drops of solvent (CH_3OH, H_2O or DMF) were added to the grinding mixture. Formation of the solid products **1**, **2** and **3** was confirmed by comparison of the experimental XRPD patterns with those calculated on the basis of the single crystal structures. **2b**: dinicotinic acid and DABCO in 1 : 2 stoichiometric ratio were also ground in an agate mortar for 20 min. The ground mixture was added to hot CH_3OH, in which it proved to be sparingly soluble, and the suspension was filtered. The clear solution was left to slowly evaporate in the air at room temperature. Good quality colourless crystals were obtained after 1 d.

Solution synthesis. *Compound 1*: $isoH_2$, (33.2 mg, 0.2 mmol) was dissolved in 5 mL of MeOH at 60 °C; to this solution DABCO (22.4 mg, 0.2 mmol) was added and well mixed, yielding a white precipitate. The precipitate was dissolved in CH_3OH and heated until a clear solution was obtained, which was left to slowly evaporate in the air at room temperature; colourless needle-shaped single crystals suitable for X-ray diffraction were obtained after 3 d. *Compound 2*: $dinH_2$ (33.4 mg, 0.2 mmol) was dissolved in CH_3OH at 60 °C; to this solution DABCO (22.4 mg, 0.2 mmol) was added and well mixed; tiny crystals formed immediately. The precipitate was dissolved in CH_3OH and heated until a clear solution was obtained, which was left to slowly evaporate in the air at room temperature; colourless needle-shaped single crystals suitable for X-ray diffraction were obtained after 2 d. *Compound 3*: $dipH_2$ (33.4 mg, 0.2 mmol) was dissolved in CH_3OH at 60 °C. To the hot clear solution DABCO was added (22.4 mg, 0.2 mmol) and the mixture was heated for 5 min. The clear solution obtained was left to slowly evaporate in the air at room temperature; colourless needle-shaped single crystals suitable for X-ray diffraction were obtained after 2 d. All the above described reactions were repeated with DMF and H_2O instead of CH_3OH; in all cases good quality crystals were obtained, whose cell parameters were matching those of the crystals obtained from CH_3OH solutions.

Crystallographic data: **1**, $C_{14}H_{18}N_2O_4$, $M_w = 278.30$, colourless needle, $0.38 \times 0.26 \times 0.22$ mm, orthorhombic, *Pbcn*, $a = 17.216(3)$, $b = 6.674(1)$, $c = 23.473(5)$ Å, $V = 2697.0(8)$ Å^3, $Z = 8$, $D_c = 1.371$ g cm^{-3}, $\mu = 0.101$ mm^{-1}, $2\theta_{max} = 58°$, 3078 total reflections, $R_1 = 0.0575$, w$R_2 = 0.1145$ for 1276 reflections ($I > 2\sigma(I)$). **2a**, $C_{26}H_{34}N_6O_8$, $M_w = 558.59$, colourless needle, $0.32 \times 0.22 \times 0.18$ mm, monoclinic, $C2/m$, $a = 21.223(2)$, $b = 6.675(1)$, $c = 10.304(1)$ Å, $\beta = 116.45(1)°$, $V = 1306.9(3)$ Å^3, $Z = 2$, $D_c = 1.419$ g cm^{-1}, $\mu = 0.107$ mm^{-1}, $2\theta_{max} = 58°$, 1695 total reflections, $R_1 = 0.0428$, w$R_2 = 0.1030$ for 981 reflections ($I > 2\sigma(I)$). **2b**, $C_{19}H_{33}N_5O_6$, $M_w = 427.50$, colourless needle, $0.23 \times 0.16 \times 0.13$ mm, triclinic, $P\bar{1}$, $a = 9.3743(7)$, $b = 10.3573(6)$, $c = 12.2042(7)$ Å, $\alpha = 84.468(5)$ $\beta = 83.268(5)$, $\gamma = 67.587(7)°$, $V = 1086.2(1)$ Å^3, $Z = 2$, $D_c = 1.307$ g cm^{-3}, $\mu = 0.098$ mm^{-1}, $2\theta_{max} = 56°$, 5046 total reflections, $R_1 = 0.0677$, w$R_2 = 0.1984$ for 2930 reflections ($I > 2\sigma(I)$). **3**, $C_{13}H_{17}N_3O_4$, $M_w = 279.30$, colourless needle, $0.38 \times 0.24 \times 0.20$ mm,

agent in the synthesis of molecular sieves and molecular perovskites.[8]

Results and discussion

For the purpose of this study DABCO was ground with each aromatic polycarboxylic acid in both dry conditions and in the presence of a catalytic amount of solvent (kneading). In all cases, the formation of co-crystals was confirmed by comparing the X-ray powder diffraction (XRPD) patterns of the polycrystalline solid products with those calculated on the basis of single crystals of the corresponding compounds prepared by conventional solution crystallization.

In the reaction between DABCO and isophthalic acid the reactants were manually ground together in an agate mortar in a 1 : 1 molar ratio for *ca.* 30 min. The XRPD pattern of the product was recorded and found to differ from those of the reactants. Formation of the co-crystal DABCO·isoH$_2$ (**1**) was confirmed by comparison of the experimental XRPD pattern of the mechanochemical product with that computed on the basis of the single crystals of **1**, which were prepared by dissolving the reactants in 1 : 1 ratio in a mixture of DMF–H$_2$O solution, followed by slow evaporation of the solvent.

The potential effect of a catalytic amount of solvent on the co-crystal formation was also explored by kneading DABCO and isoH$_2$ in the presence of CH$_3$OH or dimethyl formamide, DMF. In both cases the co-crystal was again obtained (see Fig. 1).

Crystal structure analysis of **1** revealed that isoH$_2$ and DABCO form a 1 : 1 co-crystal. The acid and base molecules in the crystal are alternatively connected *via* O(H)···N hydrogen bonds (O···N 2.56(3) and 2.58(3) Å) to yield a zigzag chain. Adjacent chains are stacked yielding the chevron-like motif shown in Fig. 2a. Within the stacking, which is two-layers thick (see Fig. 2b), the isophthalic acid molecules are arranged in "herring-bone" fashion, as it can be appreciated from Fig. 2c.

orthorhombic, *Pnma*, $a = 10.275(1)$, $b = 7.122(1)$, $c = 17.450(1)$ Å, $V = 1277.0(2)$ Å^3, $Z = 4$, $D_c = 1.453$ g cm^{-3}, $\mu = 0.109$ mm^{-1}, $2\theta_{max} = 58°$, 1671 total reflections, $R_1 = 0.0546$, w$R_2 = 0.0943$ for 1292 reflections $(I > 2\sigma(I))$.

Single-crystal data for compounds **1–3** were collected on an Oxford X'Calibur S CCD diffractometer equipped with a graphite mono-chromator (Mo Kα radiation, $\lambda = 0.71073$) and operated at room temperature. SHELX-97[12a] was used for structure solution and refine-ment on F^2, PLATON[12b] and SCHAKAL99[12c] were used for hydrogen bonding analysis and molecular graphics, respectively. Powder data were collected with a Panalytical X'Pert Pro equipped with X'Celerator detector. A Cu anode was used as X-ray source at 40 kV and 40 mA. The program PowderCell 2.2[12d] was used for calculation of the X-ray powder patterns.

Rietveld refinements: diffraction patterns in the 2θ range 5–95° were collected on a PANalytical diffractometer with Bragg-Brentano geom-etry (Cu Kα radiation, detector: X'celerator, step size $\Delta 2\theta = 0.0167°$, counting time per step = 100 s). Rietveld analyses were conducted starting from the crystal structures obtained from single crystal data, and treating all molecules/ions as rigid bodies. Shifted Chebyshev functions with 6 parameters were used to fit the background. TLS matrices were used for the acid molecules and the anions, while for the rigid body in neutral or protonated DABCO units an overall thermal parameter was adopted. Refinements of grinding experiment products converged to an R_p of 10.17% and 7.78% for compounds **1** and **2a**, respectively. Relatively high reduced χ^2 values (153.7 and 55.83, respectively) were probably due to insufficient resolution of the powder patterns.
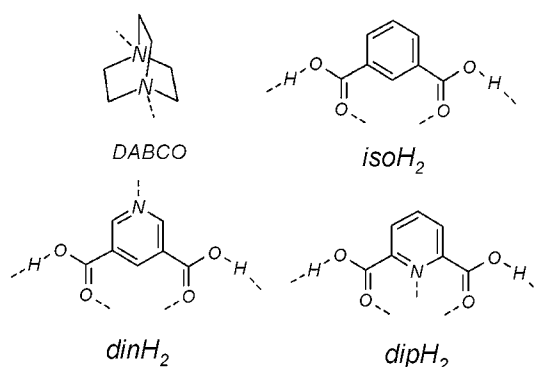

Chart 1 The solid reactants used in the current study: 1,4-diazabicyclo-[2.2.2]-octane (DABCO), isophthalic acid (isoH$_2$), dinicotinic acid (dinH$_2$) and dipicolinic acid (dipH$_2$). Dashed lines show the potential hydrogen bonding sites.

Similar grinding/kneading experiments were carried out with dinicotinic acid (dinH$_2$) and dipicolinic acid (dipH$_2$) (Chart 1). In addition to the –COOH groups, these acids also possess pyridine N-atoms that can act as hydrogen bond acceptors.

Compound **2a** was prepared by direct grinding of DABCO and dinH$_2$ in a 1 : 1 stoichiometric ratio. As for **1**, the formation of a new compound was inferred by comparing the XRPD pattern of the product with those of the starting materials. Compound **2a** was also prepared by crystallization from CH$_3$OH, and the XRPD pattern calculated on the basis of single crystal data is superimposable to the one measured on the product of the solid-state reaction (see Fig. 3). The same product was obtained *via* kneading experiments in the presence of cata-lytic amounts of CH$_3$OH and DMF (see Fig. 3).

Crystal structure analysis shows that **2a** is a salt, and that negative and positive ions in this solid are "supramolecular anions" and "supramolecular cations", respectively (see Fig. 4a). The [(dinH$_2$)(dinH)]$^-$ monoanion is formally constituted of a neutral acid molecule and one hydrogen dinicotinate anion, joined together by a very short O···H···O hydrogen bond (O···O 2.45(2) Å), whereas the [DABCO-H-DABCO]$^+$ monocation is
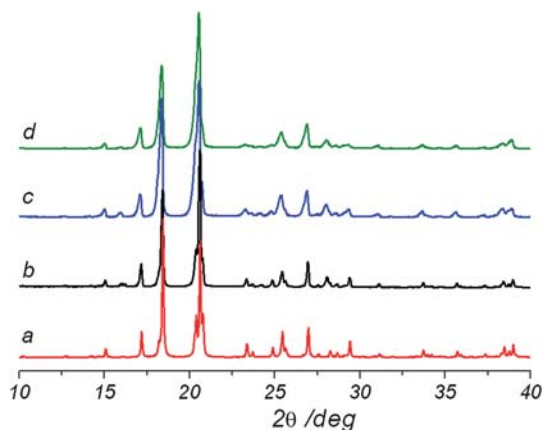

Fig. 1 Compound **1**: comparison between the XRPD pattern calculated on the basis of single crystal data (a) and those measured on the solid products obtained by grinding (b) and kneading with CH$_3$OH (c) and DMF (d).

formally constituted of a neutral base molecule and one monoprotonated DABCOH⁺ cation joined by a short N···H···N hydrogen bond (N···N, 2.71(2) Å). The carboxylic groups on the anionic dimer interact *via* O(H)···N hydrogen bonds with the free N-acceptor sites on the cationic dimers (O···N, 2.56(2) Å), thus forming a 1D chain extending along the *c*-axis (see Fig. 4). Both nitrogen atoms on the anionic dimer are involved in C(H)···N hydrogen bonding interactions (C···N 3.52(3) Å) connecting adjacent chains, as shown in Fig. 4b.

A search in the Cambridge structural database (CSD[9]) yielded only three compounds[10] in which the [DABCO-H-DABCO]⁺ cationic dimer is present (GATMAP01, RULFAF, ROHTAJ), as shown in Fig. 5. The most frequently occurring motif, apart from [DABCOH]⁺ or [DABCOH₂]²⁺ single-moiety cations, is the [DABCOH]ₙⁿ⁺ infinite cationic chain; a trimeric unit of the type [HDABCO-HDABCOH-DABCOH]⁴⁺ was only found in a bromide salt (DAHGUO01). A search on salts containing systems similar, in size and hydrogen bonding functions, to the [DABCOH]⁺ cation, *e.g.* the piperazinium and pyrazinium cations, showed that, in all cases where monocations are present,
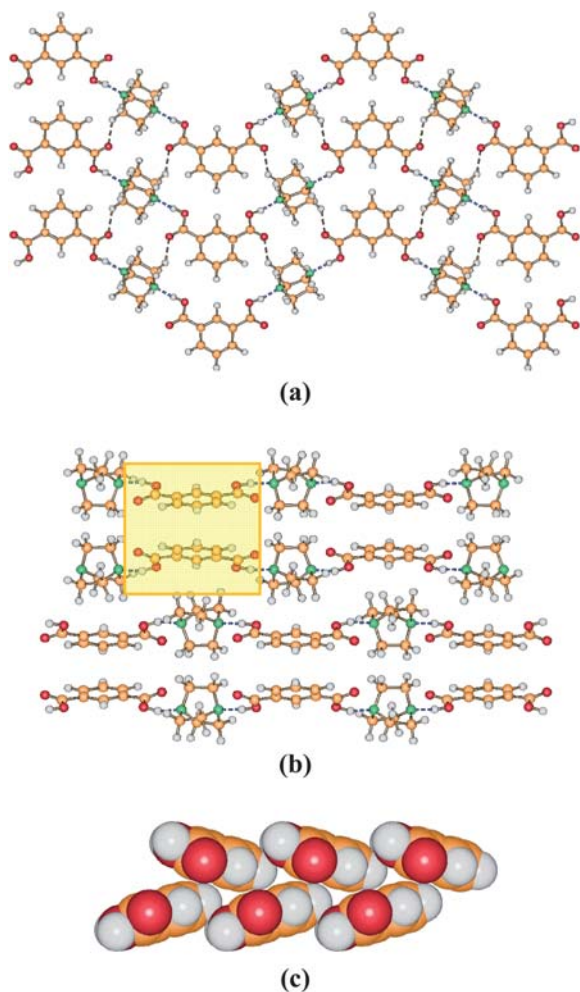

Fig. 3 Compound **2**: comparison between the XRPD pattern calculated on the basis of single crystal data (a) and those measured on the solid products obtained by grinding (b) and kneading with CH₃OH (c) and DMF (d).

Fig. 4 "Supramolecular" cations and anions (a) alternating and forming chains in crystalline **2** *via* O(H)···N hydrogen bonds, (b) view in the *ac*-plane.

Fig. 2 (a) The chevron-like arrangement of isoH₂ and DABCO observed in the co-crystal **1** along the *a*-axis. (b) A front view (along the *b*-axis) of the same packing arrangement, showing the stacking of two such layers, and (c) a side-view enlargement showing the herring-bone pattern of isophthalic acid molecules within the stacking.
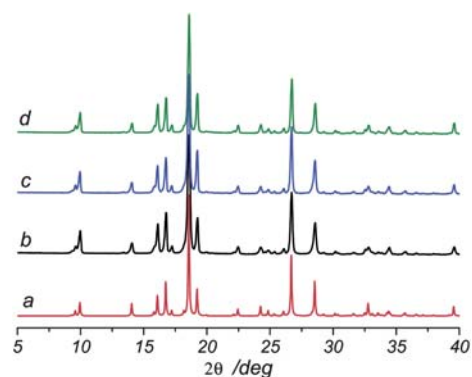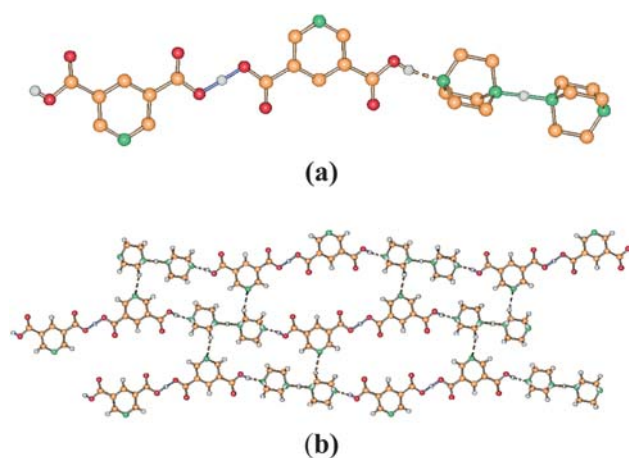
infinite chains are observed, and only for the pyrazinium salt QEFBEI a [pyr-H-pyr]⁺ dimer can be identified (N···N 2.766 Å).

Different stoichiometric ratios were also tried in the case of **2a**, to see whether it was possible to obtain a different form, in which the dimeric units were disrupted. Both dinH₂:DABCO in the 1 : 2 and 2 : 1 ratios were mixed in solution, but upon recrystallization (either from CH₃OH and DMF) compound **2a** was invariably obtained.

The experiment was then performed again by kneading the reagents in the presence of a catalytic amount of solvent (CH₃OH): the powder pattern of the resulting solid shows a different profile from that of compound **2a**. The polycrystalline product was dissolved in the minimum amount of warm methanol; evaporation of the clear solution yielded single crystals of compound **2b**, whose pattern matches that of the kneading product (see Fig. 6).

Compound **2b** is a dehydrated form, and contains a completely deprotonated dinicotinate dianion and two monoprotonated [DABCOH]⁺ units. Both carboxylate groups on the dinicotinate dianion are hydrogen bonded to the –NH⁺ groups of the two the [DABCOH]⁺ cations and to two water molecules [N(H)···O_COO–
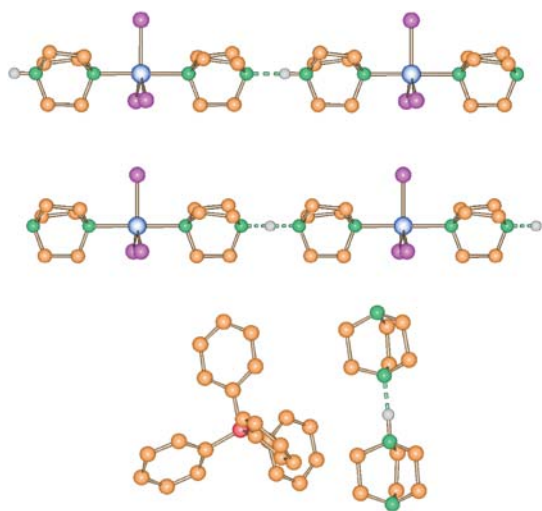
Fig. 5 "Supramolecular" [DABCO-H-DABCO]+ cationic dimers in (from top to bottom) GATMAP01, RULFAF, ROHTAJ. N–(H)–N distances are 2.658, 2.658 and 2.698 Å for the [CuCl₃]⁻, GATMAP01, the [NiCl₃]⁻, RULFAF, and the [BPh₄]⁻, ROHTAJ, salts, respectively.

2.657(3) and 2.683(3) Å, $O_{COO-}\cdots(H)O_{water}$ 2.768(4) and 2.721(3) Å], as it can be seen in Fig. 7a. The two water molecules are also hydrogen bonded to each other [$O_{water}(H)\cdots O_{water}$ 2.811(4) Å. The two [DABCOH]+ cations interact with each other *via* a C(H)···N hydrogen bond [$C_{CH}\cdots N$ 3.384(4) Å]. Fig. 7b shows the simultaneous interaction of the [DABCOH]+ cations with the anions and the water molecules in the crystal [N···(H)O_{water} 2.875(3) Å].

In the case of dipH₂ a similar reaction with DABCO yielded the 1 : 1 molecular salt **3**. As in crystalline **1** the main packing feature is the alternation of [DABCOH]+ and hydrogen dipicolinate ions, interacting *via* N+(H)···O⁻ hydrogen bonds (N···O 2.56(2) and 2.59(2) Å), as shown in Fig. 8; a short bifurcated C(H)···O interaction involving the C=O group of the carboxylic moiety and a –CH₂ group on the [DABCOH]+ cation [C···O 2.87(2) Å] is also visible in the figure. This short interaction is

probably responsible for the fact that the resulting hydrogen bonded chain in **3** is much more "wavy" with respect to the zigzag chain observed in crystalline **1**.

The comparison between the powder diffraction pattern obtained from single crystal data and those measured on samples obtained by grinding and kneading with CH₃OH and DMF is reported in Fig. 9.

As it can be seen from Fig. 9, the powder pattern profile (b), *i.e.* that one measured on the product of the grinding reaction, contains some contaminant peaks, not present in the calculated pattern. In order to verify the presence of additional phases, either due to unreacted solids or to different solid products, we decided to recur to a more quantitative analysis in the form of Rietveld refinements.

The software GSAS[11] was used for the refinements, since it allows a "rigid body" Rietveld analysis. Experimental and difference patterns, together with Rietveld plots, are shown in Fig. 10. All peaks in the experimental patterns of **1** (Fig. 10a) and **2a** (Fig. 10b) could be explained by the refined phases (except for a low intensity peak in compound **1**). Rietveld refinement of the grinding experiment product for compound **3** was not completed, since we found peaks that could not be justified by any known phase or mixture of phases (see Fig. 10c); this new phase might well be an intermediate of the solid state grinding process. Unfortunately, we were not able to characterize it, as we did not succeed in growing crystals suitable for single-crystal X-ray diffraction.

A reason for the co-crystal/molecular salt formation upon reaction with DABCO, on passing from isophthalic to dipicolinic
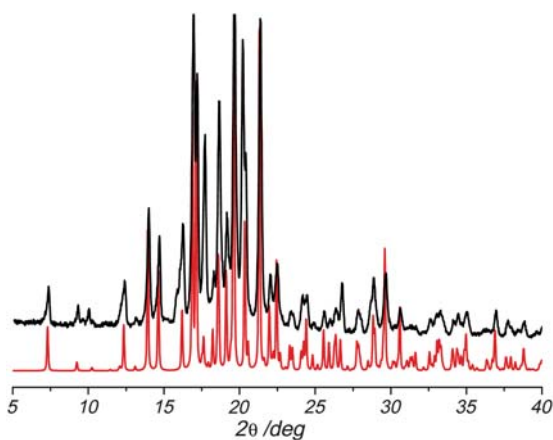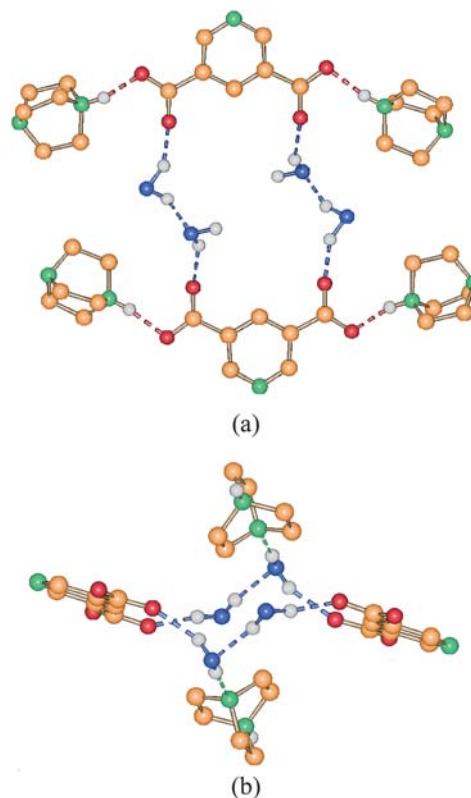

Fig. 6 Compound **2b**: comparison between the XRPD pattern calculated on the basis of single crystal data (red profile) and those measured on the solid product obtained by kneading with CH₃OH (top, black profile).

(a)

(b)

Fig. 7 Hydrogen bonding motifs connecting the dinicotinate dianion, the [DABCOH]+ units and the water molecules in compound **2b**.
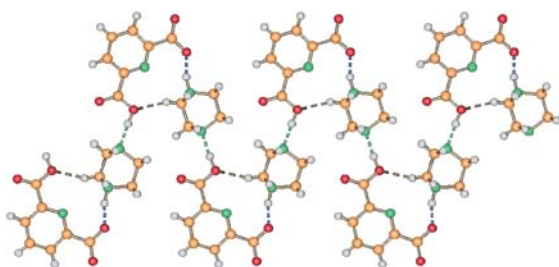
Fig. 8 Alternation of molecular anions and cations in crystalline **3**, forming a wavy hydrogen bonded chain along the *b*-axis.
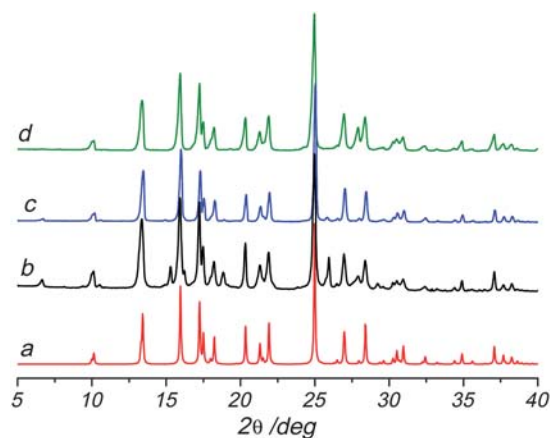

Fig. 9 Compound **3**: comparison between the XRPD pattern calculated on the basis of single crystal data (a) and those measured on the solid products obtained by grinding (b) and kneading with CH_3OH (c) and DMF (d).

Fig. 10 Experimental pattern, calculated pattern and difference curve for Rietveld refinements of compounds **1** (a), **2a** (b) and **3** (c) as obtained by grinding processes. Stars indicate peaks that could not be attributed to any known phase.

acid, is probably to be found in the pK_a trend observed for the three acids. Although pK_a values are strictly valid for reactions in solution, they should still be responsible for the formation of hydrogen bonded supramolecular aggregates in solution, which then grow into their respective solids. For example, the acid $dipH_2$, with the highest value of $pK_1 = 2.16$ undergoes mono-deprotonation with formation of a 1 : 1 salt with DABCO, while $dinH_2$, with a $pK_1 = 2.80$, shows deprotonation of one –COOH group every two acid molecules, and isophthalic acid, with the lowest pK_1 value of 3.54, remains in its protonated form, co-crystallizing with neutral DABCO. In the solid state reaction yielding compound **2b**, however, deprotonation of the dinicotinic acid is made possible by the excess of DABCO: the same reaction, however, does not occur in solution, even if the 1 : 2 stoichiometric ratio is used. Acidity and basicity, again, are concept to be used carefully when comparing the results of solution or solid state reactions.

In conclusion, we have prepared by grinding and kneading techniques four novel co-crystals/salts of DABCO with aromatic dicarboxylic acids that are topologically similar to each other. Single crystals of all solids were obtained by conventional crystallization methods allowing full characterization of the crystalline materials. The structural analysis made possible to distinguish between molecular salts and co-crystals formation. In all cases, 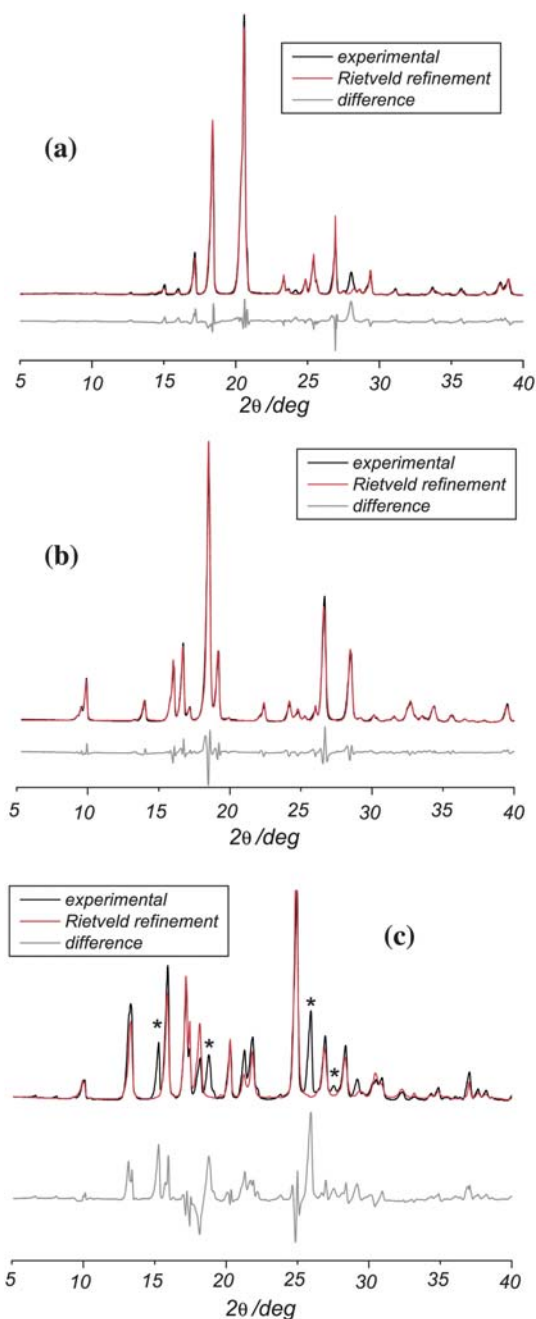except for **2b**, the solid products were consistently obtained also when the preparation (*e.g.* grinding or kneading) and/or the crystallization conditions were varied; crystalline **2b** could only be obtained by kneading.

The difference in packing motifs between **2** and those of **1** and **3**, which are more closely related in spite of the different topology, brings in the question of polymorphism, *i.e.* whether different crystal forms of the species discussed herein could exist. In particular those similar to **2**, which contains "dimeric" DABCO units could be formed also with the other acids. This aspect will be the subject of future investigations.

Acknowledgements

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