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ARTICLE

Ex-situ and *in-situ* monitoring of the syntheses of thermochromic Schiff bases

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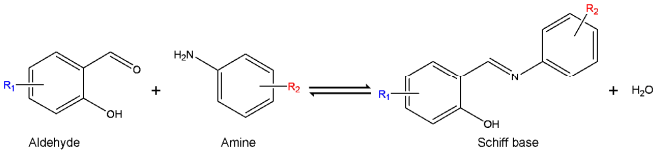
Schiff bases derived from *o*-hydroxy aldehydes were obtained by mechanochemical synthetic methods with a liquid or a paste present as an intermediate phase. The effectiveness of this procedure was monitored by means of *ex-situ* PXRD and DSC, respectively. In case of four Schiff bases, *in-situ* PXRD study was also conducted in order to monitor the synthesis of the product formed by merely putting the amine and the aldehyde in close contact. One of the *o*-hydroxy Schiff base appears in two polymorphic forms. The monoclinic polymorph has been reported previously in the literature (herein obtained by the solution based method using methanol) while the synthesis and characterisation of the triclinic form is now reported (obtained by neat grinding or using acetonitrile during recrystallization). The reversible thermochromic properties in the solid state were also investigated in the temperature range from 298 to 110 K. The structural reasons of such behaviour were thoroughly reasoned.

Introduction

The Schiff bases or imines can be effortlessly obtained by condensation of aldehydes (or ketones) and primary amines[1] and thereafter used as ligands in coordination chemistry of transition metals.[2] Besides, the imines (and their coordination compounds) are widely recognised compounds that possess biological and pharmacological properties[3] and, as was shown recently, they can be used as anionic receptors.[4] On the other hand, the research of prosperous methods of synthesis such as mechanochemical ones provides new insights into faster and ecologically and economically more acceptable ways to prepare new but also already known compounds. [5] Various Schiff bases have been obtained in such manner by neat (**NG**), liquid-assisted (**LAG**) and seeding-assisted (**SEAG**) grinding.[2,6] There are three general mechanisms of the mechanochemical synthesis of organic compounds: (*i*) molecular transport across surfaces, through vapour phase or through the bulk of a crystal[6(a)], (*ii*) formation of liquid eutectic intermediate phases[6(c),7] and (*iii*) reaction *via* an amorphous intermediate phase.[8] An *ex-situ* PXRD study had recently revealed that the relative humidity (RH) plays an important role in the formation of the Schiff bases in the solid state. One could assume that the lower the RH the conversion of the aldehyde and amine into an imine and water (Scheme 1) will be favoured. However, a study of Cinčić *et al.* showed that it is not so and that the moisture actually acts as a catalyst in this solid state reaction.[9]



Scheme 1 General procedure of aromatic Schiff base synthesis

Perhaps one of the most beautiful aspects of chemistry is the colour change of the reaction mixture upon aging. Even more unusual and at the same time intriguing are the changes in the colour of the synthesized substances by altering the physical parameters of the environment: temperature, pH, polarity of the solvent polarity, ionic strength etc.[10] Among the organic compounds that exhibit reversible photo- and/or thermochromic properties in the solid state, the Schiff bases are particularly important.[11-14] Generally speaking, there are roughly three (mutually dependent) reasons for the thermochromic behaviour of the imines in the solid state: (*i*) proton transfer *via* intramolecular O···N hydrogen bond and consequently the change of the tautomeric form,[11] (*ii*) at the temperatures below room temperature, the colour change of thermochromic crystals is dominated by the contribution of fluorescence and not only by the contribution of light absorption, which is due to the shift of the tautomeric equilibrium[13] and (*iii*) the stereochemistry of the molecule, *i.e.* its planarity or amount of deviation from planarity in correlation with the crystal packing.[11,12] For items (*i*) to (*iii*) it is also crucial that the imine is derived from an

o-hydroxy aldehyde so that an intramolecular O···N hydrogen bond is present.[11-14]

According to the literature, for the imine to be thermochromic in the solid state, the dihedral angle closed by the best planes in which the aromatic systems of the aldehyde and amine moiety lie should be $\Phi < 25°$. The molecules are then closely packed in their crystal lattice due to π···π and/or C–H···π interactions.[14(a),14(b)] However, the first examples of controversy regarding the correlation of the dihedral angle and the chromic phenomena were two non-planar thermochromic Schiff bases derived from benzylamine in 1987.[12(a)] In addition, it has been considered up until then that thermo- and photochromism are mutually exclusive.[11] The example of *N*-4-methoxy--salicyilidenebenzylamine was the first one in this class of compounds to show both properties and to put the planarity/nonplanarity hypothesis into revision.[12(a)] Furthermore, the more recent studies on Schiff bases derived from aminopyridines[14(a)] and aminomethylpyridines[14(b)] confirm that the planarity of the molecule is an independent structure parameter that should not be taken into consideration when predicting the chromic properties of the *o*-hydroxy Schiff bases. This all indicates that the studies of the thermo- and photochromism of Schiff bases in the solid state should be continued.

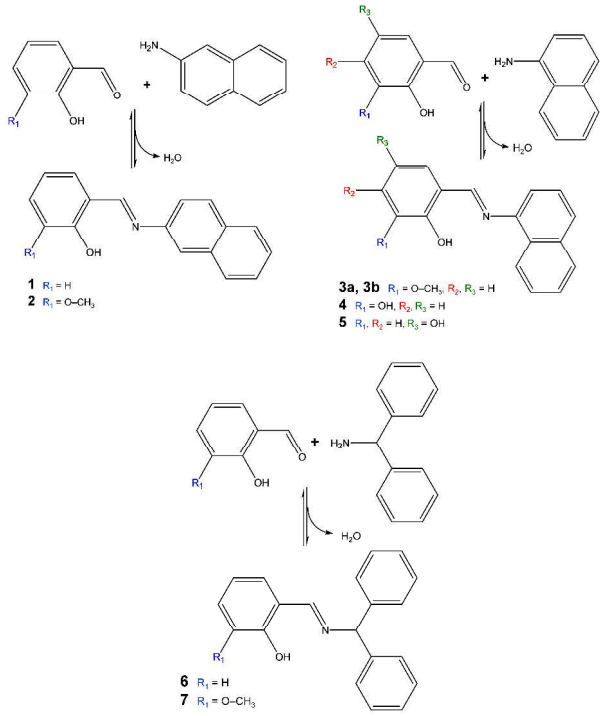
Herein, we report the study of the mechanochemical methods of synthesis of the Schiff bases and, to the best of our knowledge, the first *in-situ* powder X-ray diffraction (PXRD) monitoring of their formation. The thermochromic properties of the prepared compounds were also thoroughly investigated.

Results and discussion

The syntheses and *in-situ* and *ex-situ* monitoring of their advancement by PXRD

The compounds **1** to **7** (the IUPAC names are listed in Table S1) were obtained by condensation of *o*-hydroxy aldehyde and amine (Scheme 2) by mechanochemical methods except of **3b**[15] obtained by the solvochemical method. Due to different colouration, and in some cases aggregation states of the reactants and the product, the advancement of the synthesis can be readily monitored by naked eye or a camera as can be seen from Fig. 1.

The required grinding time in the agate mortar was determined empirically when the colour of the reaction mixture stopped to change. The results of the PXRD experiments point out that compounds **1**, **3a**, **4** and **6** were successfully synthesized by neat grinding in the agate mortar (**NGam**) (Fig. S15 to S21). The traces of the reactants are present in the **NGam** powder product of the synthesis of **2** and **5**. Compund **2** was therefore synthesized by means of neat grinding in a ball mill (**NGbm**). Neither **NGam** nor **NGbm** were successful enough to obtain pure **5**, so liquid-assisted grinding in the agate mortar (**LAGam**) was used (Fig. 2).



Scheme 2 Molecular schemes of the syntheses of compounds **1** to **7**.

The reactants used in the syntheses of **1**–**7** differ in the physical state. Nevertheless, all products were obtained as solid powders. In the synthesis of **1** and **7** one of the reactants is a solid and the other is a liquid, and in obtaining of **6** both reactants were liquid. In these three cases the role of grinding is to mix the reactants so that the passive product surface cannot slow or prevent the advancement of the reaction. In the case of **7** a catalytic amount of ethanol was added in order to accelerate the solidification of the reaction mixture after seven minutes of grinding. In all other syntheses both reactants were solids. At the same time, in all seven cases a liquid paste is present as an intermediate phase (Fig. S1 to S7).

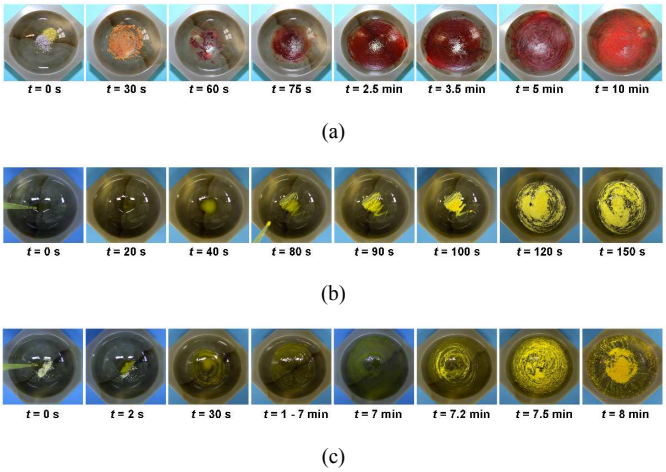


Fig. 1 NG syntheses of (a) **5**, (b) **6** and (c) **LAG** synthesis of **7** in a mortar.

Since the reactants have low melting points (or are liquids at room temperature) the possible mechanism of the formation of

these was proposed earlier.[7] In this case grinding acts to create a high interfacial area between the starting solid phases at which the liquid phase can form.

The shear induced by the grinding and the contact between the liquid or paste-like intermediate phase and the residual solid surfaces then induces the nucleation and growth of the product from the liquid phase.[7(c)] The intermediate phase is metastable and it solidifies by further usage of the mechanical force,[14(c)] by changing the temperature,[7(a),(b),(e)] by adding a catalytic amount of liquid as in case of compound **7** or a very small crystal of the desired product or polymorph that acts as a nucleus of the crystallization (solidification).[6(a),16]

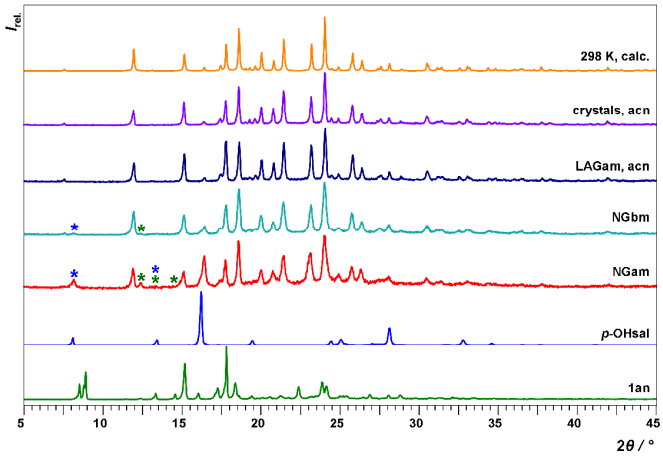


Fig. 2 The PXRD patterns of the reactants (***p*-OHsal** and **1an**) and the powder products obtained by means of neat grinding in the agate mortar (**NGam**) and in the ball mill (**NGbm**), respectively and by liquid-assisted grinding in the agate mortar (**LAGam**) compared to the patterns of the recrystallized material and the calculated pattern.

The *in-situ* PXRD monitoring was performed for **2**, **3**, **4** and **5** because the reactants for their synthesis are solids. As can be seen from Fig. 3, a paste is formed after about 2 minutes in the **NG** preparation of **2** (Fig. 3 (a)), **4** (Fig. 3 (c)) and **5** (Fig. 1 (a)) while a liquid is formed after about 1 minute in the preparation of **3** (Fig. 3 (b)). However, there are crucial differences between the results of grinding and "close contact" syntheses.

The first diffraction maximum of **2** at approx. 25° 2θ appears 9 minutes after the reactants were gently mixed with a spatula and put into the sample holder (Fig. 3 (d)). The diffraction maximum of ***o*-van** at approx. 26° 2θ disappears after 13 minutes. Nevertheless, the maxima of **2an** are present in the pattern even after one day and can be attributed to the white needle-like crystals that can be seen on the surface of the red product in the sample holder. The intensity of the maxima of the reactants ***o*-OHsal** and **1an** at 8.5°, 8.8° and 8.9° 2θ deteriorate severely in first 10 minutes after they were put into close contact but remain present even after 3 days and can be attributed to the pale purple and light red domains that can be seen on the surface of the dark red product in the sample holder. The first diffraction maximum of **4** appears after about 30 minutes. It is not easy to give details for contact reaction of ***p*-OHsal** and **1an** since there is only one diffraction maximum (at *cca.* 12° 2θ) that does not overlap with the maxima of reactants (Fig. S23). The performed *in-situ* experiments for compound **5** indicate that the maximum at 12.2° 2θ is present even in the first diffraction pattern taken in the first minute and increases slightly with time (Fig. S28). The overall crystallinities in the formation of **2**, **4** and **5** are more-or-less preserved pointing to a difference in the mechanism of the formation by grinding and by only putting the reactants in close contact. The appearance of the paste-like intermediate phase in the grinding experiments indicates to the mechanism of the formation of the liquid (eutectic) interphase while the "close contact" reaction more probably goes *via* diffusion of the molecules of the reactants through the reaction mixture.[6(a)-(c), 7]

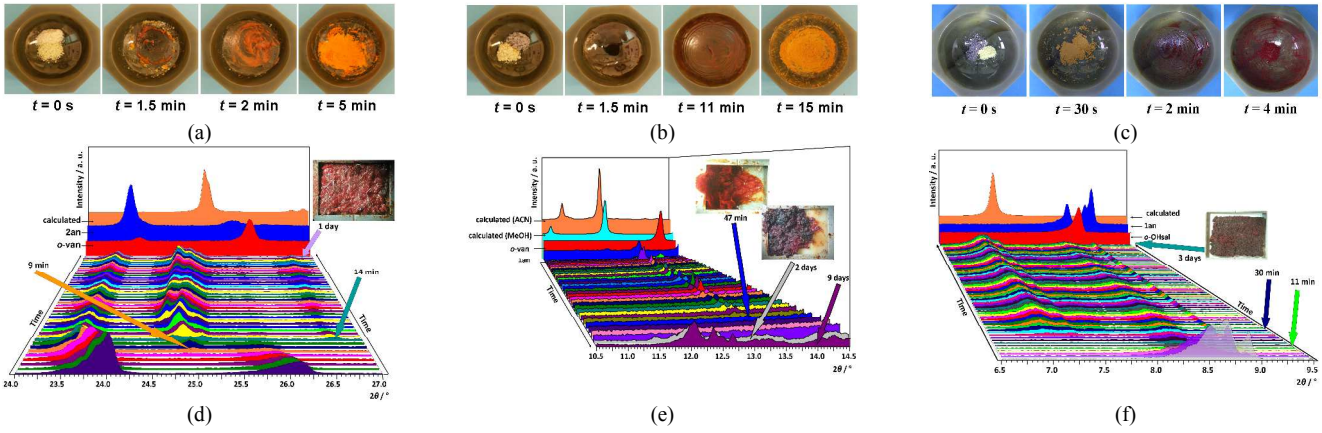


Fig. 3 The changes during the synthesis of (a) **2**, (b) **3a** and (c) **4** by **NG**. The PXDR patterns observed by *in-situ* monitoring of the formation of (d) **2**, (e) **3b** and (f) **4**. [Time headed (d) and (f) from and (e) towards the reader for better visibility.]

In the case of the contact reaction of ***o*-van** and **1an** the amorphization of the reaction mixture starts almost immediately (Fig. 3 (e)) and the reaction mixture is completely amorphous after 47 minutes. This is in good agreement with the formation of the liquid in the grinding experiment and with the proposed mechanism (*via* an intermediate liquid or paste-like intermediate).[7] The reaction mixture solidifies in 2 days but the pattern changes slightly during nine days. Diffraction maxima in 2θ range in Fig. 3 (e) could not undoubtedly be attributed to either triclinic **3a** or monoclinic polymorph **3b**. Due to the fact that PXRD pattern in 2θ range 5° to 45° was recorded and the patterns were compared to the patterns of the recrystallized material from **acn** and **MeOH** (Fig. S26). The only conclusion that can be made is that **3b** is the more probable product in this simple contact reaction. The fact that goes in favour to this statement is the diffraction maximum at $2\theta \approx 5.5°$. Thus, **3a** can be obtained by neat grinding and/or (re)crystallization from acetonitrile while **3b** can be obtained from methanol or probably by simple contact reaction of the reactants.

The broadening of the diffraction peaks can be noticed in the *in-situ* PXRD patterns and attributed to the formation of particles smaller in size than the size of the particles of reactants used and/or the microstrains caused by the migration of the molecules in the crystal.[17]

Crystal and molecular structure v.s. thermochromism in the solid state

Reversible thermochromic properties of the prepared imines were studied in the temperature range 298 to 110 K. The tautomer present in the solid state was determined according to: (*i*) either C2–O1 and C7–N1 bond length criterion[18] or (*ii*) the position of the hydrogen atom (H1) located from the electron density map (Fig. S8 to S14 b)) or both (*i*) and (*ii*) simultaneously. Bond length values were calculated using own SCXRD structural data and data deposited in the CSD.[19] The values of O1–C2 and N1–C7 bond lengths and of the dihedral angles between aromatic rings for **1**–**7** are comprised in Table S9. The geometric parameters of the intermolecular contacts are listed in Table S10.

Compound **1**,[20] **3a** (all four crystallographically independent molecules), **5** and **7** are enol-imines at both temperatures used. Rather diffused electron density in the region of chelate ring intra-molecular O···N hydrogen bond of **6**[21] implies to the presence of keto-enol tautomeric equilibrium at both temperatures (Fig. 4 b)). Nevertheless, the existence of enol-imine tautomer only in the solid state of **6** is confirmed by the limiting values of C2–O1 and C7–N1 bond lengths. The change from a pure tautomer to the keto-enol tautomeric equilibrium and *vice versa* is observed in **2** and **4**.[22] Compound **2** is an intrinsic enol-imine at 298 K. At 110 K both forms are present in the tautomeric equilibrium with 0.74 : 0.26 ratio in favour of enol-imine in **2** (Fig. 4 a)). The keto-enol tautomeric equilibrium in **4** with prevalence of the keto-amine form (0.67 : 0.33) at 298 K disappears entirely at 110 K in favour of keto-amine tautomer. The results of the FT-IR spectroscopic experiments (Fig. S39 to S42 and Table S12) point to probable co-existence of both tautomers in the solid state in all cases. These results could not unambiguously be used for tautomer selection. The data obtained by means of NMR spectroscopy indicate that all seven compounds are enol-imines in the DMSO solution regardless of the tautomeric form in the solid state (Fig. S43 to S46 and Tables S13 and S14).

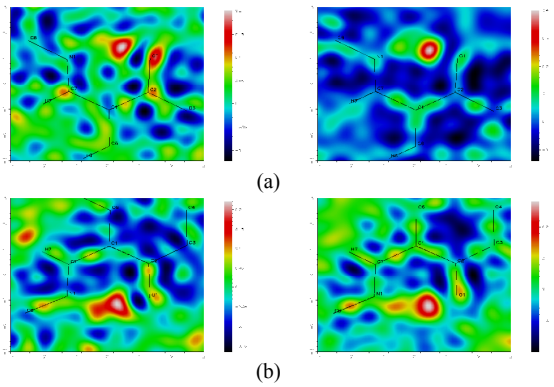


Fig. 4 δF maps calculated in the domain of N1–C7–C1–C2–O1 chelate ring of (a) **2** and (b) **6** at RT (left column) and LT (right column).

The formation of the supramolecular motifs in all compounds is dominated by C–H···O, C–H···π and π···π interactions. However, an O–H···O type H-bond is also present in **4** and **5**. The molecules of **5** and **7** form 1D-helices *via* *y* and *z* crystallographic axis, respectively. The molecules of **2** are interconnected by means of three C–H···O interactions forming 1D-helix *via* *y* crystallographic axis. These 1D-helices are interconnected by an additional C–H···O H-bond into a 2D supramolecular network. The O–H···O and C–H···O interactions put the molecules of **4** in a close contact in such a manner that the pairs of dimers are formed. The dimers form 1D-chains *via* *x* crystallographic axis by C–H···O and π···π interactions. The molecules of **3a** form a 3D supramolecular network through weak C–H···O type hydrogen bonds. There is no special supramolecular motif in **1** and **6**. Therefore, the molecules simply repeated in 3D space by means of the space group symmetry elements. The packing diagrams of the compounds reported within this publication for the first time are presented in Fig. S15 to S18.

The appealing thermal behaviour of **2**, **3a**, **3b**, **4**, **6** and **7** can be observed from the photographic pictures of the crystals shown in Fig. S47 to S54. In addition, compound **6** shows negative

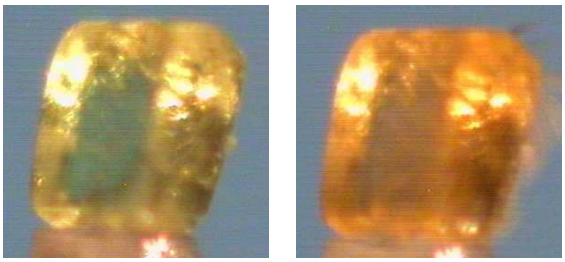


Fig. 5 Photographs at (a) RT and (b) LT showing negative solid state thermochromism of **6**.

thermochromism, a phenomenon of deepening of the colour upon cooling which is rarer than the positive one (Fig. 5). Compounds **1** and **5** do not change their colour upon cooling or the colour change cannot be observed by human eye in temperature range used.

The stereochemistry of aromatic Schiff bases (*i.e.* their planarity defined through the value of angle between best planes of aldehyde and amine ring moieties, the dihedral angle Φ) and the thermochromic behaviour are in great discrepancy with the hypothesis that the Schiff bases with non planar molecules cannot show such a phenomenon.[11] Thus, based on the increasing evidence on the molecular structure of Schiff bases through the years, the dihedral angle showed to be an independent factor that should not be taken into consideration when discussing about chromic behaviour of the Schiff bases. It has been reported previously that the value of the dihedral angle should be $\Phi < 25°$ for a Schiff base to be thermochromic.[14(a),(b)] The mentioned angle in **1** is around 8° (Table S11) but does not change its colour with temperature. The value of the angle in **2** is 14° and it is thermochromic. The average value of the dihedral angles (four crystallographically independent molecules in the asymmetric unit) in **3a** is around 25° (going form *cca.* 22° to 33° at RT) and the compound is thermochromic in the solid state. The angle is around 10° in monoclinic polymorph **3b**[15] and it changes its colour with temperature although not so dramatically as **3a**. The aromatic subunits of the molecules of **4** are mutually inclined at an angle of 5° and the thermochromism is present. Compound **5** does not show thermochromic properties and the angle is 55°, way beyond 25°. Hitherto, the thermochromic properties of the Schiff bases derived from **adpm** have not been reported. These molecules cannot be planar due to the existence of a CH spacer group between the aromatic ring that originates from an *o*-hydroxy aldehyde and the two phenol groups that originate from the amine. Therefore, the negative thermochromic properties of **6** and positive thermochromism of **7** are evidences that Schiff bases with fairly non planar molecules ($\Phi > 60°$) can be thermochromic in the solid state. The degree of non-planarity of the molecules of **1**–**7** can be easily perceived in Fig. 6 showing molecular overlap.

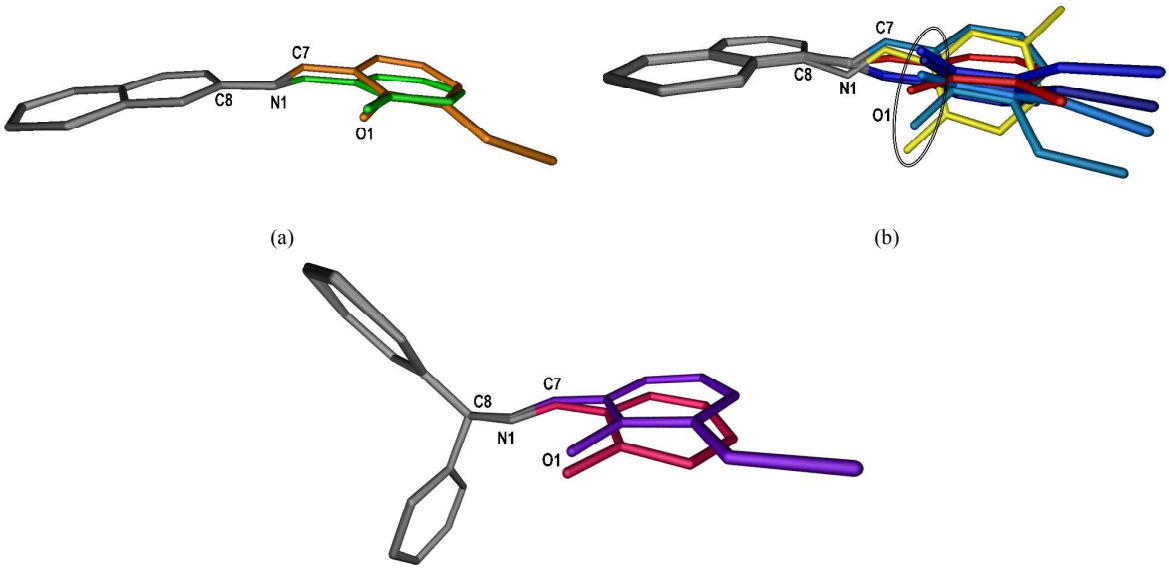


Fig. 6 Overlapping pictures of (a) **1** and **2**, (b) **3a**, **4** and **5**, and (c) **6** and **7**. In all drawings the plane of aromatic amine moiety was overlapped. In the case of compound **6** and **7** the planes of both phenyl rings are overlapped.

The *ex-situ* DSC monitoring of the efficacy of the mechanosynthesis

The results of *ex-situ* DSC and PXRD experiments performed on the powder product of the conducted method of synthesis and on the recrystallized material are mostly in good agreement with. The differences are in the case of **4** and **7.** In the DSC thermogram of the **NGam** powder product in case of the synthesis of **4**, one can see a weak peak with an onset at 111 °C that originates from the melting of the traces of unreacted ***o*-OHsal.** Furthermore, such peak with the onset on 78 °C point to the traces of ethanol used in the synthesis in the case of **7.** These traces certainly cannot be found in the *ex-situ* PXRD diffraction patterns. The DSC and TGA thermograms are presented in Fig. S28 to S38.

Experimental

Synthesis

The mechanochemical syntheses were performed by grinding equimolar quantities of aldehyde and amine (1 mmol : 1 mmol) in an agate mortar (Fig. S1 to S7) and the efficacy was monitored *ex-situ* by PXRD as described in the literature.[14(c)] The IUPAC names of **1**–**7** are listed in Table S1. The syntheses

of **2** and **5** were repeated in a Retsch MM200 grinder mill operating at 25 Hz frequency for 30 minutes. The monoclinic polymorph[15] of the compound **3** was obtained by solution (methanol) based synthesis.

In order to monitor the advancement of the reaction using *in-situ* PXRD merely by putting the reactants in close contact, equimolar quantities of aldehyde and amine (1 mmol : 1 mmol) were gently mixed in a mortar with a spatula to provide homogeneity of the reaction mixture and to ensure no (or minimal) mechanic force to be used. The reaction mixture was transferred into an aluminium holder, evened and then put into the instrument.

The single crystals for single crystal X-ray diffraction experiments (SCXRD) were obtained by recrystallization and evaporation from small amount of solvent [compounds **1**[20] and **6**[21] – acetone (**ace**), **3a** and **5** – acetonitrile (**acn**), **2** – tetrahydrofurane (**thf**), **3b**[15] – methanol (**MeOH**), **4**[22] – chloroform (**chl**) and **7** – ethanol (**EtOH**)].

The X-Ray Diffraction Measurements

Crystal and molecular structures were determined at 298 and 110 K using SCXRD on an Oxford Diffraction Xcalibur Kappa CCD X-ray diffractometer with graphite-monochromated MoK_α (λ = 0.71073 Å) radiation (for details see ESI).[23] The data concerning the results of the crystallographic experiments are listed in Table S2 to S8. Further details are available from the Cambridge Crystallographic Centre.[24]

In order to monitor the efficacy of the synthetic method used and to qualitatively identify the products (Fig. S19 to S25) the powder X-ray diffraction (PXRD) experiments were performed on a PHILIPS PW 1840 X-ray diffractometer with Cu$K_{\alpha 1}$ (1.54056 Å) radiation at 40 mA and 40 kV. The scattered intensities were measured with a scintillation counter. The angular range (2θ) was from 5 to 45° with steps of 0.02°, and the measuring time was 0.5 s per step in the case of the *ex-situ* experiments.

In the case of the *in-situ* monitoring of the contact reaction of *o*-vanillin (***o*-van**) and 2-aminonaphthalene (**2an**), the angular range (2θ) was selected according to the reactants diffraction maxima from 23.0 to 27.0° with steps of 0.02°, and the measuring time was 0.5 s per step. The measurements were repeated in 40 cycles. In the case of the *in-situ* monitoring of the contact reaction of ***o*-van** and 1-aminonaphthalene (**1an**), the angular range (2θ) was also selected according to the reactants diffraction maxima from 11.5 to 14.5° with steps of 0.02°, and the measuring time was 0.5 s per step. The measurements were repeated in 70 cycles. In the case of the *in-situ* monitoring of the contact reaction of *o*-hydroxysalicylaldehyde (***o*-OHsal**) and **1an**, the angular range (2θ) was from 6.5 to 9.5° with steps of 0.02°, and the measuring time was 0.5 s per step. The measurements were repeated in 195 cycles. In the case of the in-situ monitoring of the contact reaction of p-hydroxysalicylaldehyde (p-OHsal) and 1an, the angular range (2θ) was from 11.0 to 14.0° with steps of 0.02°, and the measuring time was 0.5 s per step. The measurements were repeated in 200 cycles. The data collection and analysis were performed using the program package *Philips X'Pert*.[25]

Conclusions

The first *in-situ* PXRD study of the synthesis of the Schiff bases is reported.

All reactants used have melting points below 120 °C, thus the reaction mixtures obtained by grinding could provide liquid intermediate phases seen in all seven cases reported herein. This indicates that the role of grinding in these seven cases is to remove the passive surface of the product from the reactants, to ensure the improvement of the contact between the unreacted reactants.[7(e)] *Ex-situ* PXRD monitoring revealed that four compounds were successfully obtained by neat grinding in an agate mortar (**1**, **3a**, **4** and **6**). More time and/or mechanic force is necessary to obtain 2 without traces of reactants in the powder product so neat ball-milling was used. To obtain **7** and pure **5** it is essential to add a very small amount of solvent while grinding in order to speed up the procedure and to improve the contact between the particles of the reactants as proposed by the mechanism. The *ex-situ* DSC experiments are mostly in good agreement with the ones obtained by ex-situ PXRD.

The in-situ PXRD monitoring of the "close contact" formation of 2 showed that the overall crystallinity of the reaction mixture is preserved during the procedure pointing to the formation of the product via diffusion mechanism.[7(c),(d)] This points out that the mechanism of the formation of **2**, **4** and **5** by grinding is not the same as in the "close contact" reaction.[7(a),(b),(e)] The *in-situ* monitoring of the synthesis of compound **3** by "close contact" revealed that the amorphization of the reaction mixture is almost immediate and the monoclinic polymorph **3b** is the more probable product.

Compounds **2**, **3a**, **3b**, **4**, **6** and **7** show vivid reversible thermochromic behaviour in the 289 to 110 K temperature range while **1** and **5** do not change their colour upon cooling or the colour change cannot be observed by human eye in temperature range used. In addition, compound **6** shows negative thermochromism, a rarer phenomenon than the positive thermochromism. The conducted crystallographic study revealed that the molecules of the prepared Schiff bases are mostly organized in the crystal by C–H···O, C–H···π and π···π interactions. Also, we have once again showed that the degree of planarity of the molecule is an independent parameter and should not be taken into consideration when discussing about thermochromism of the Schiff bases.[11-14] Nevertheless, the keto-enol tautomerism should also be revised as a reason for such behaviour.[11,12] The change in the position of the tautomeric equilibrium with the change of the temperature was proven only in case of **2** and **4** where the ratio of the keto-amine tautomeric form increases upon cooling. In the case of all other compounds the molecules are in enol-imine form.

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Notes and references

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Electronic Supplementary Information (ESI) available: [Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 973331 and 973332 for compound **2** at LT and RT, CCDC No. 973333 and 973334 for compound **3a** at LT and RT, CCDC No. 973335 and 973336 for compound **5** at LT and RT and CCDC No. 973337 and 973338 for compound **6** at LT and RT, respectively. Copies of these data may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CBZ 1EZ, UK (Fax:+44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Photographies of the grinding syntheses in the agate mortar, FT-IR spectra, ^{1}H and ^{13}C NMR spectra, DSC and TG thermograms and PXRD patterns for all relevant materials are listed in Electronic Supporting Information. See DOI: 10.1039/b000000x/

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24 Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.ac.uk or www: http://www.ccdc.cam.ac.uk). These data can be obtained free of charge from the Director upon request quoting the CCDC deposition numbers 973331–973338.
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Ex-situ and *in-situ* monitoring of the syntheses of thermochromic Schiff bases

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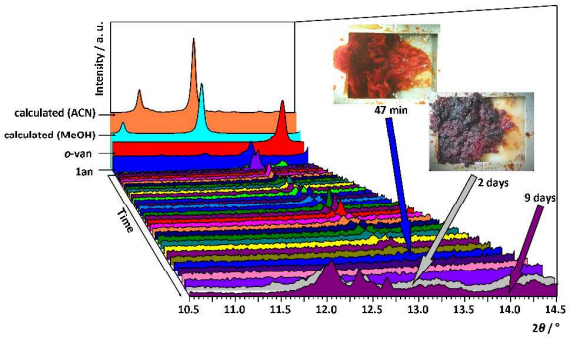

This work presents an *in-situ* PXRD monitoring of the syntheses of thermochromic Schiff bases and a study of the mechanisms of their formation.