Thermochimica Acta 507–508 (2010) 1–8

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Solvent-free preparation of co-crystals of phenazine and acridine with vanillin

Dario Braga*, Fabrizia Grepioni, Lucia Maini, Paolo P. Mazzeo, Katia Rubini

Dipartimento di Chimica "G.Ciamician", Università degli studi di Bologna, Via Selmi 2, 40126 Bologna, Italy

ARTICLE INFO

Article history:
Received 1 February 2010
Received in revised form 26 April 2010
Accepted 28 April 2010
Available online 7 May 2010

Keywords:
Co-crystal
Polymorph screening
Solvent-free reactions
Thermochemistry
Variable temperature X-ray diffraction
Hot-stage microscopy

ABSTRACT

Co-crystals of phenazine and acridine with vanillin have been obtained by solvent-free reaction or thermal treatment of the solid reactants: their structures, thermal behaviour and eutectic formation have been investigated via single crystal X-ray diffraction, differential scanning calorimetry (DSC), variable temperature X-ray powder diffraction and hot-stage microscopy (HSM). Polymorph screening of the reagents has also been carried out.

1. Introduction

The investigation of co-crystals, namely the crystalline materials obtained by the supramolecular association of two or more molecules, is at the forefront in the field of crystal engineering, because they represent a route to innovation for chemical and pharmaceutical industries [1–6]. Co-crystals often show different chemical and physical properties with respect to those of the reagents or of their mixtures; their intimate association in the solid state affects solubility, dissolution rate, chemical stability, etc. [7,8]. Undoubtedly, the most common approach exploits the hydrogen bond as the supramolecular linker of choice to bind together the molecular components; co-crystals based on acid–base pairs are particularly favoured [9,10]. On the other hand, in co-crystals formed by molecules carrying "hydrogen bonding donor" groups, i.e. –COOH, –OH, NH, etc. and molecules carrying "hydrogen bond acceptor" groups proton transfer may occur, leading to the formation of charged species, i.e. a molecular salt. There is no precise borderline between "all neutral" and "charged" hydrogen bonded systems, because the position of the hydrogen atom along the D–H···A vector depends heavily on temperature and on the time scale of the experiment used to evaluate the hydrogen position [11–13]. It is often necessary, therefore, to employ complementary techniques, such as solid state NMR, to understand the nature of the hydrogen bonding interactions in co-crystals [14,15].

In this paper we report the preparation of co-crystals of acridine and phenazine with vanillin. Phenazine, structurally related to anthracene, is an important precursor in the synthesis of dyes such as eurhodines, toluylene red, indulines and safranines [16]. Many phenazine compounds are found in nature and are produced by bacteria [17,18]. Acridine, which possesses only one N-atom, is also used as a precursor for the production of dyes [19] and some valuable drugs [20–22]. Acridine and related derivatives bind to DNA and RNA due to their abilities to intercalate [23].

We have chosen to co-crystallize these two structurally related molecules with vanillin (see Scheme 1), a co-former carrying the relatively weak –OH hydrogen bonding donor group, able to interact with the acceptor N-sites on the rings. Vanillin is a natural product extracted from the vanilla bean and, although it is mainly used as a flavouring agent in foods and beverages [24,25], recently it has been studied also for its potential anticancer effects [26,27].

This study is part of a larger investigation on the formation of co-crystals and mixed-crystals of simple substituted phenyl rings [28]. More specifically we were interested in assessing, by a combined use of single crystal and variable temperature powder diffraction and thermal techniques (DSC and HSM), whether co-crystal formation upon mechanical mixing of the reactants took place in the solid state or in the presence of a liquid intermediate (eutectic) phase. The mechanisms of mechanically activated processes are still a matter of much debate [29]. A polymorph screening on all reagents has also been carried out.

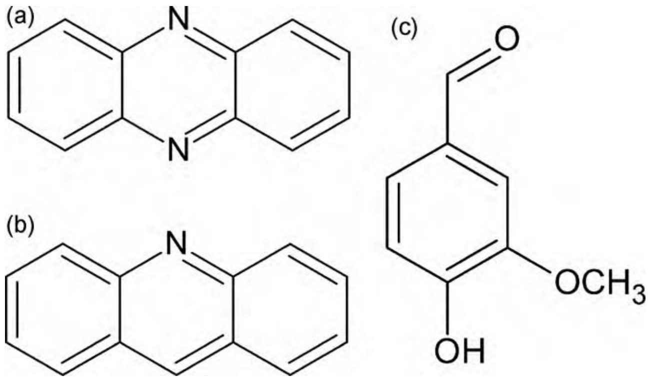
2. Experimentals

All reagents and solvents were purchased from Aldrich and used without further purification.

---

* Corresponding author. Fax: +39 051 2099456.
E-mail address: dario.braga@unibo.it (D. Braga).

0040-6031/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2010.04.021



Scheme 1. Chemical sketches of (a) phenazine, (b) acridine and (c) vanillin.

2.1. Polymorph screening

Phenazine. Phenazine was re-crystallized from different solvents: re-crystallization from ethanol, acetonitrile, THF, dioxane and toluene invariably yielded pure form α, while concomitant formation of α and β have been observed from dichloromethane and pure form β was re-crystallized form nitromethane.

Re-crystallization of phenazine from hydrochloric acid 1N yields crystals of phenazine hydrate, while from hydrochloric acid 15N red crystals of phenazine hydrochloride are obtained.

Acridine. Re-crystallization of acridine from ethanol, acetonitrile, THF, dioxane and toluene yielded form II; form III was obtained from dichloromethane and ethyleneglycoldimethyl ether, while form IV was obtained from DMSO. Re-crystallization of acridine from p-xylene resulted in the concomitant formation of forms II and IV.

Vanillin. Re-crystallization of vanillin from ethanol, acetonitrile, dichloromethane, p-xylene, THF, dioxane, toluene and nitromethane yielded form I, while form II was obtained from isopropyl alcohol.

2.2. Slurry experiments

Thermodynamic stability of phenazine was established by stirring a saturated solution of phenazine in nitromethane in presence of both α and β solid forms. After 1 month the solid phase was recovered and was characterized as pure form β.

2.3. Synthesis of co-crystals **1** and **2**

Co-crystallization of phenazine and vanillin in solution has been obtained by dissolving 0.1 mmol (0.018 g) of phenazine and 0.2 mmol (0.030 g) of vanillin in the minimum amount (∼4 mL) of toluene required to obtain a clear solution with no solid residue; long needles, suitable for X-ray single crystal measurements, were obtained after 1 day by slow evaporation at 70 °C.

Crystals suitable for X-ray-analysis of **2** have been obtained after 6 h by slow evaporation at 4 °C of 5 mL of a solution of dichloromethane in which 0.1 mmol of acridine (0.018 g) and 0.1 mmol of vanillin (0.015 g) had been dissolved.

2.4. Grinding experiments

Phenazine (0.1 mmol, 0.018 g) and vanillin (0.2 mmol, 0.030 g) were manually ground for 15 min in an agata mortar; an X-ray powder diffraction measurement on the solid product showed formation of pure co-crystal **1**.

Acridine (0.2 mmol, 0.036 g) and vanillin (0.1 mmol, 0.015 g) were manually ground for 15 min in an agata mortar: an X-ray powder diffraction measurement on the solid product showed the presence of a physical mixture of the starting compounds; even grinding of the reagents in the presence of a drop of water was not successful, and co-crystal **2** could not be obtained.

2.5. Heating experiments

Co-crystal **2** was obtained by heating the reaction mixture acridine/vanillin in 2:1 molar ratio above the eutectic temperature of the mixture, and leaving the melt to recrystallize in the air at ambient conditions.

2.6. Crystal structure determination

Crystal data were collected on a Oxford Xcalibur S with Mo-Kα radiation, λ = 0.71073 Å, monochromator graphite. Crystal data and details of measurements are summarized in Table 1. SHELX97 [30] was used for structure solution and refinement based on F^2. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon atoms were added in calculated positions. Mercury [31] was used for the graphical representation of the results. The program PLATON [32] was used to calculate the hydrogen

Table 1
Crystal data and details of measurements for the forms III–IV of acridine and co-crystals **1** and **2**.

Form	Acridine III	Acridine IV	1	2
Formula	$C_{13}H_9N$	$C_{13}H_9N$	$C_{28}H_{24}N_2O_6$	$C_{17}H_{14}NO_2$
Mol wt	179.21	179.21	484.49	528.58
System	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$	$P2_1/n$	Pnma
a (Å)	6.0693(2)	6.1788(5)	4.0265(2)	13.296(1)
b (Å)	18.8181(7)	15.719(2)	35.240(2)	17.836(1)
c (Å)	16.2830(5)	29.312(3)	8.4977(6)	11.6104(7)
α (°)	90	90	90	90
β (°)	95.155(3)	90	101.134(6)	90
γ (°)	90	90	90	90
V (Å^3)	1852.2(1)	2846.8(5)	1183.1(1)	2753.4(3)
Z'	8	12	2	4
Density (g cm^{-3})	1.285	1.254	1.360	1.275
F(000)	752	1128	508	1112
μ(MoKα) (mm^{-1})	0.075	0.074	0.097	0.084
Measured reflns	18,654	12,535	7031	6350
Unique reflns	4333	5880	2629	2117
Refined parameters	254	380	167	200
GOF on F^2	0.914	0.860	1.123	1.116
R_1 (on F, $I > 2\sigma(I)$)	0.0472	0.0524	0.0621	0.0984
WR$_2$ (F^2, all data)	0.0950	0.0815	0.1481	0.1428

bond distances. CCDC 763816–763821 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

2.7. *Powder diffraction measurements*

X-ray powder diffractograms were collected on a Panalytical X'Pert PRO automated diffractometer with Cu Kα radiation and an X'Celerator detector equipped with an Anton Paar TTK 450 low-temperature camera. The program PowderCell 2.2 [33] was used for calculation of X-ray powder patterns on the basis of the single crystal structure determinations.

2.8. *Differential scanning calorimetry (DSC)*

The measurements were performed using a PerkinElmer Pyris Diamond DSC equipped with a model ULSP 90 intra-cooler. Temperature and enthalpy calibrations were performed by using high purity standards (n-decane and indium).

The samples (3–5 mg) were placed in aluminium hermetic pans. Heating was carried out at 5 °C min^{-1} in the temperature range from 25 to 190 °C.

2.9. *Hot-stage microscopy (HSM)*

Contact preparations for optical microscopic experiments were crystallized under controlled temperature on a glass slide; heating temperatures in the range −50 to 190 °C were applied according to the desired final crystal form. An Olympus BX41 polarization microscope equipped with a hot-stage Linkam LTS 350 was used, controlled by the Linksys32 software, and the samples were heated at different rates according to the experiment. An Infinity 1 camera connected to the microscope was used to take pictures of the samples, and these have been analyzed with the Infinity Analyze software.

3. Results and discussion

3.1. *Co-crystals of phenazine:vanillin and acridine:vanillin*

Co-crystals of phenazine:vanillin 1:2 (**1**) have been prepared by direct grinding of the solid reactants and from solution (see Section 2).

Comparison (see Fig. 1) between the powder diffraction pattern measured on the bulk material of the solvent-free reactions and that calculated on the basis of single crystal data shows that the solvent-free reaction is quantitative and yield the same product as that obtained from solution.

The structure of solid **1** is constituted of distinct supramolecular adducts formed by one phenazine and two vanillin molecules. The two vanillin molecules lye almost orthogonal to the phenazine plane and are connected each via an O(H)···N hydrogen bond [O···N 2.875(2) Å] to the two nitrogen atoms on the phenazine. The phenazine molecules are stacked along the *a*-axis via π···π interactions, with a distance between their planes of 3.37 Å, while distances between the centroids of N-containing rings (in red and green in Fig. 2b) are 3.51 Å (Fig. 3).

The mono-hydrated co-crystal acridine:vanillin 1:1 (**2**) could not be obtained by simple mechanical mixing of the solid reagents. The structural characterization was conducted on single crystals obtained from dichloromethane. Analogously to what observed in solid **1**, crystalline **2** is also constituted of discrete supramolecular adducts formed by two acridine and one vanillin molecules, linked together via one water molecule, as shown in Fig. 4b. Two distinct molecular layers are detectable in the packing: the first is constituted only of vanillin and water molecules, while the second contains the acridine molecules (see Fig. 4c and d). It is noteworthy that the acridine molecules arrange themselves preserving the same π···π stacking interaction that is also present in the form II of pure acridine.

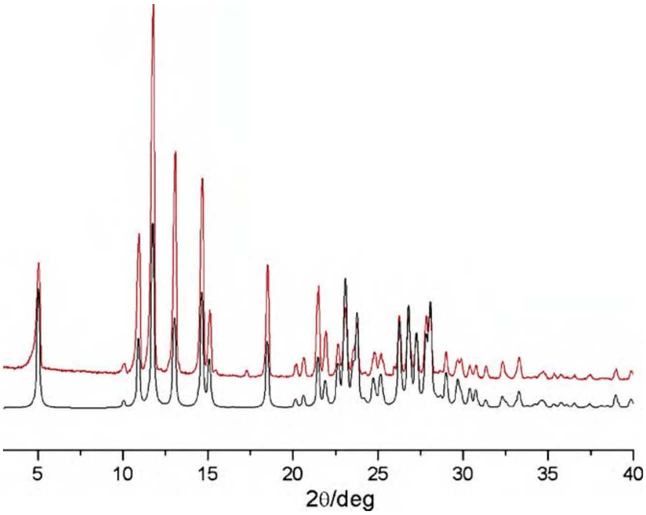


Fig. 1. Co-crystal **1**: comparison between the XRPD pattern calculated on the basis of single crystal data (bottom) and the one measured on the product of the solvent-free reaction (top).

3.2. *Thermal characterization*

Thermal analysis of **1** has been carried out by differential scanning calorimetry (DSC), variable temperature X-ray powder diffraction (VT-XRPD) and hot-stage microscopy (HSM).

The DSC analysis of **1** shows an endothermic peak at 88 °C, which is attributed to the melting of **1** also observed via HSM.

It has been possible to show that the co-crystal is generated via formation of a eutectic phase, as can be shown by HSM experiments. Two single crystals of phenazine and vanillin were placed in contact and heated on the hot-stage device (Fig. 5). Melting of the eutectic is visible at 79 °C, and at 50 °C on cooling the co-crystal crystallizes as needles.

The formation of the co-crystal was observed also in the contact preparation method for HSM reported in the literature [34]. First a small amount of the higher melting component is melted on the hot stage, so that it covers about half the area between a coverslip and a glass slide, then it is cooled down and allowed to solidify. The lower melting component is then placed on the other half of the glass slide and melted: when the vanillin melts, the liquid gets in contact with solid phenazine and formation of the co-crystal **1** is observed.

In Fig. 6a it is possible to distinguish three zones characterized by different composition: from left to right we can identify vanillin form I, co-crystal **1** and phenazine α. On heating to 77 °C (Fig. 6b) the eutectic between vanillin (left) and **1** (middle) melts, then at 80 °C vanillin also melts (Fig. 6c) and finally at 84 °C the co-crystal **1** melts (Fig. 6d). On cooling to 75 °C it is possible to observe re-crystallization in needles of co-crystal **1** (needles in Fig. 6e, f).

A DSC characterization of **2** could not be made, as no pure form of the co-crystal could be obtained.

The formation of crystalline **2** was observed in contact mode on the HSM. The process, visually represented in Fig. 7, differs from the one observed for **1**. Melting and re-crystallization of vanillin, which is now the higher melting form, results in the formation of

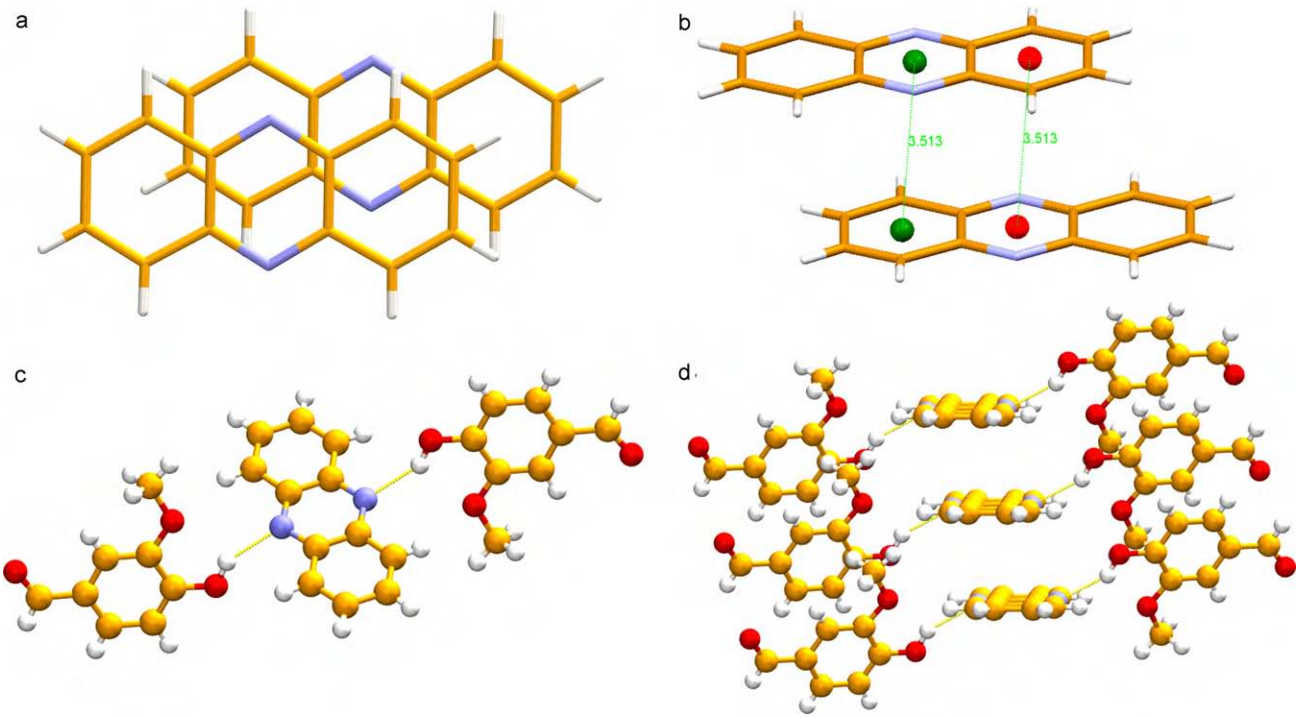


Fig. 2. Crystalline **1**: (a) perspective view which shows the shift of the two molecules of phenazine; (b) $\pi\cdots\pi$ interactions and distances between centroids for the same molecules (front view); (c) O(H)···N interactions linking one phenazine and two vanillin molecules; (d) $\pi\cdots\pi$ stacking of phenazine molecules.

two different solid phases (spherulite and rectangular plates in the left part of Fig. 7a); on the right side of Fig. 7a acridine is visible. Co-crystals of **2** formed after 24 h, and constitute the central brown strip in Fig. 7a. On heating, at 55 °C the eutectic between the vanillin and **2** melts (Fig. 7b), while the co-crystal melts at 63 °C (Fig. 7c, d).

A variable temperature X-ray powder diffraction experiment on the physical mixture of acridine:vanillin in a 2:1 ratio shows that only the reagents are present at RT. Upon heating to 55 °C, melting of the eutectic form can be seen. Contrary to what observed for **1**, the eutectic phase does not recrystallize as co-crystals of **2** until

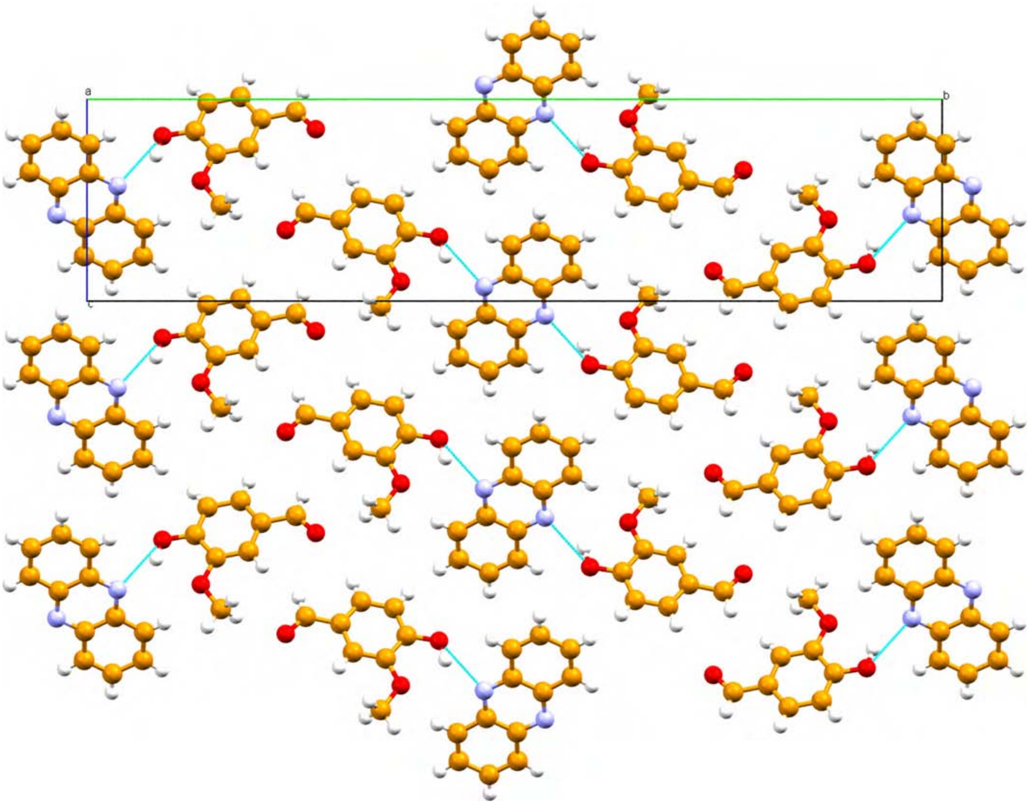


Fig. 3. View of the packing along the *a*-axis in crystalline **1**.

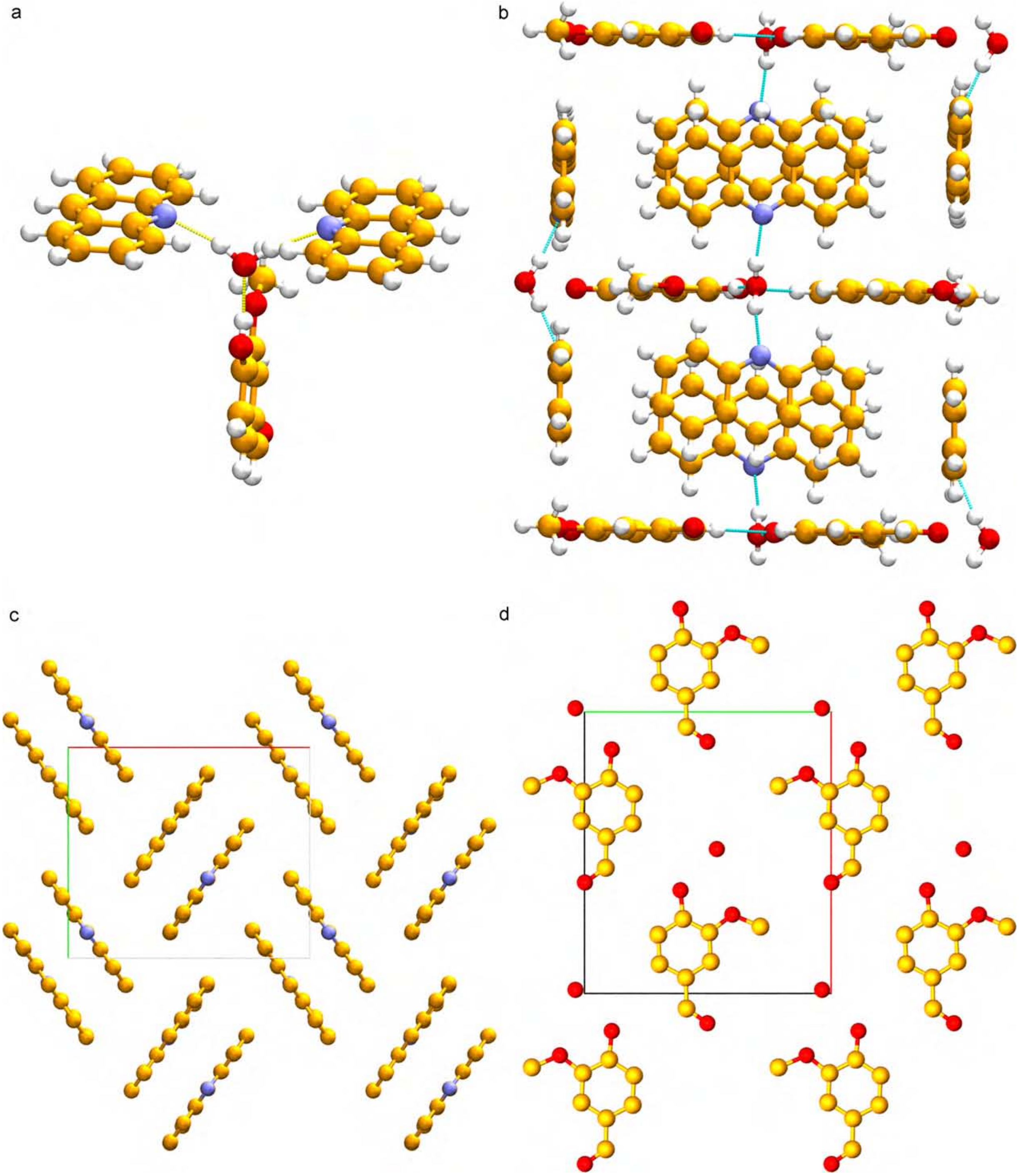


Fig. 4. Crystalline **2**: (a) the water molecule acts as a link between two acridine and one vanillin molecules via hydrogen bonding; (b) view of the packing along the *a*-axis; (c) layer consituted of acridine molecules, (d) layer consituted of vanilline and water molecules.

mechanical stress with a glass rod is applied at RT; what is more, reagents can still be detected in the final solid mixture. It is worth noting that crystalline **2** is a monohydrate, as water is stoichiometrically absorbed from the air during the crystallization process (Fig. 8).

Grinding together acridine and vanillin, or kneading them in the presence of a drop of water, did not result in formation of the co-crystal, as evidenced by X-ray powder diffraction, which shows the presence of a physical mixture of the reagents; this is quite surprising, giving the low melting point of the eutectic between acridine/vanillin and that locally temperature can increase considerably as an effect of the mechanical grinding.

3.3. *Polymorph screening of phenazine, acridine and vanillin*

A polymorph screening of the reagents has also been carried out, which consists of re-crystallization of the compounds at RT from different solvents and from melt (see Section 2). Two polymorphs of phenazine have been found, according to literature [35–37,38]. Liquid phenazine re-crystallizes as form α, which is the commercial form. By a slurry experiment in nitromethane (see Section 2) it was possible to establish that the β form is the thermodynamically stable form at RT. Form β is obtained by slow evaporation of nitromethane, while from all the other solvents employed only form α is obtained. Re-crystallization of phenazine from solutions

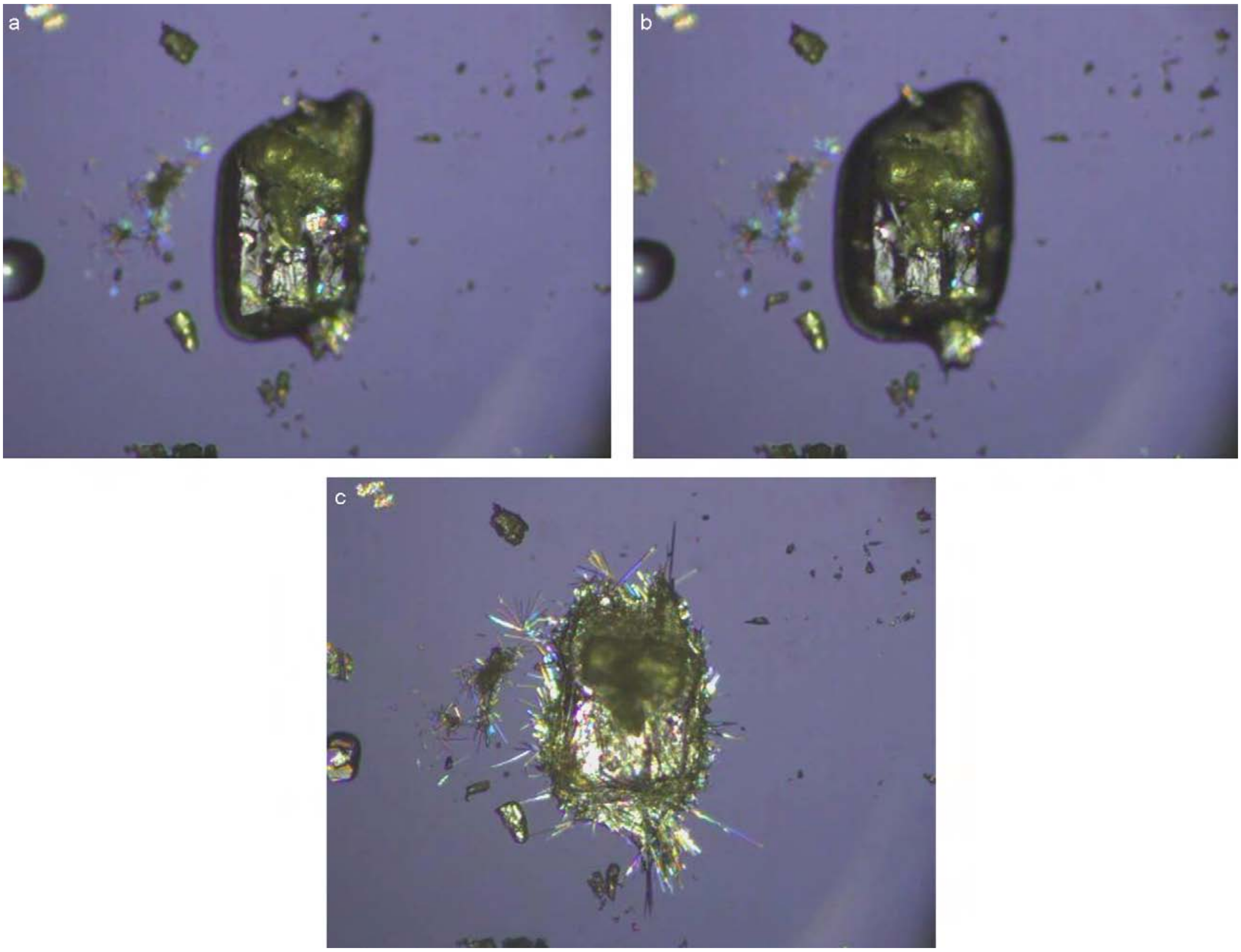


Fig. 5. Crystals of phenazine (top) and vanillin (bottom in close contact): (a) 78 °C, on heating; (b) 79 °C, on heating; (c) 50 °C, on cooling.

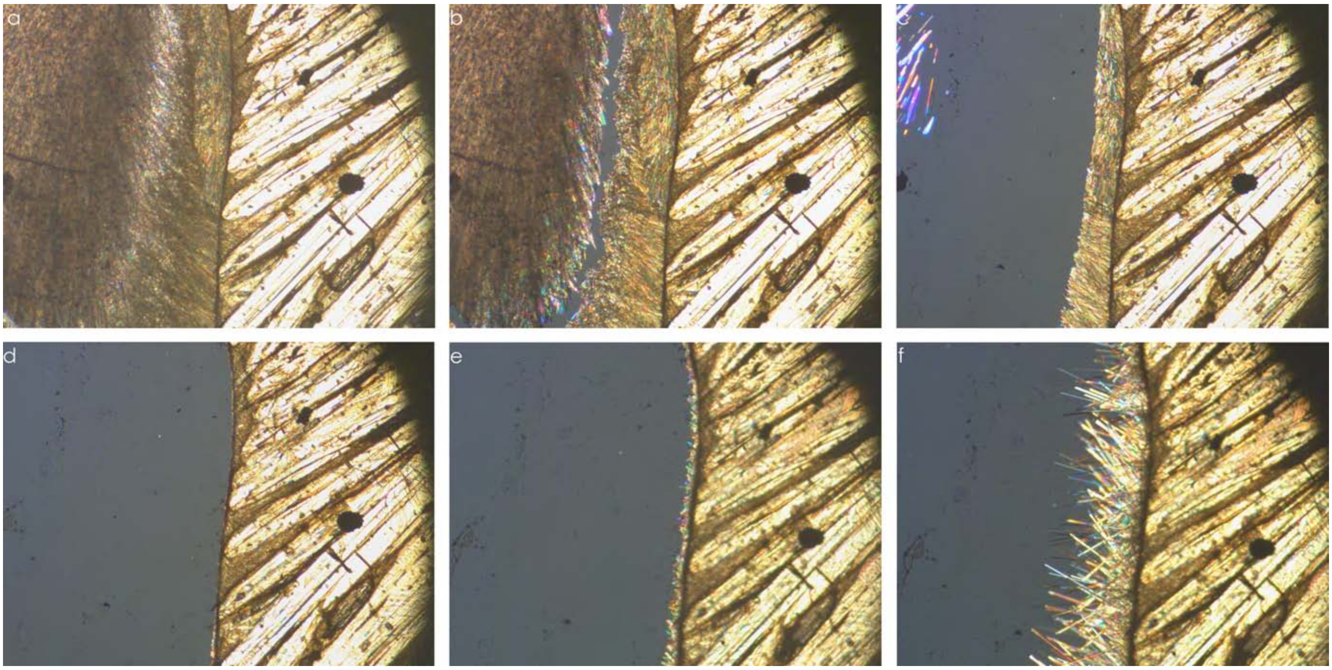


Fig. 6. HSM analysis of vanillin and phenazine in contact mode: (a) 76.8 °C, on heating; (b) 77 °C, on heating; (c) 80.5 °C, on heating; (d) 84 °C, on heating; (e) 75.4 °C, on cooling; (f) 65 °C, on cooling.

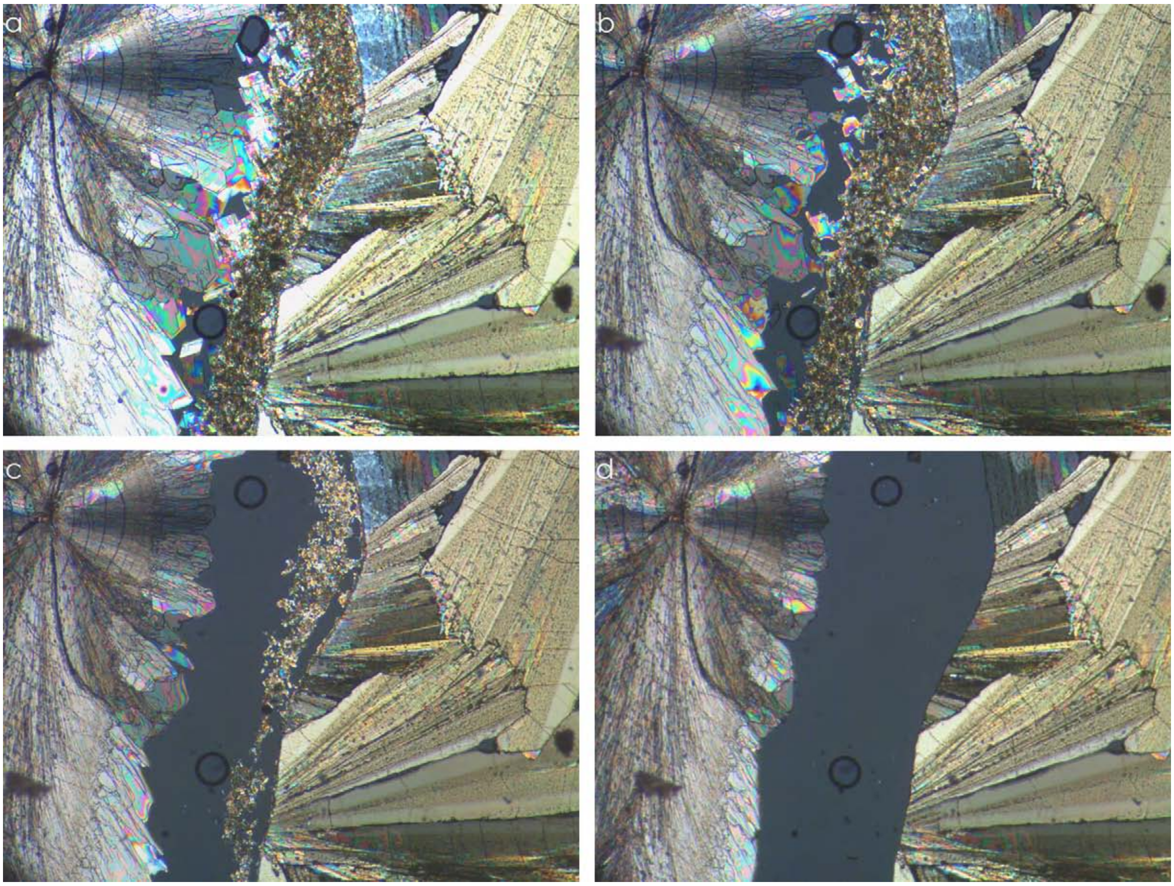


Fig. 7. HSM analysis of vanillin and acridine in contact mode: (a) 37 °C, on heating; (b) 55 °C, on heating (melting of the eutectic phase); (c) 63 °C, on heating (melting of co-crystal **2**); (d) 68 °C, on heating (only vanillin and acridine are left).

of hydrochloric acid at different concentrations yielded crystals of phenazine hydrate and phenazine hydrochloride, for which we report the structural characterization as supplementary material.

Three polymorphs of acridine out of the six reported forms[39,37,40–42] have been found by polymorph screening. Phase transition temperatures are listed in Table 2; the nomenclature is consistent with the one reported in the CSD [43].

Crystal structures of polymorph III and IV, obtained from dichloromethane and DMSO, respectively, have been redetermined, since in the CSD low quality data are deposited (see supplementary material).

Form III is the commercial form and form II is the thermodynamically stable form at RT, as reported in the literature. Re-crystallization from melt yielded form II. Form II transforms, with an endothermic event, into a new high temperature form at 101 °C which we named form VIII; this solid-state transition is more visible in samples obtained from melt than in samples obtained by re-crystallization from solvent. The two polymorphs are enantiotropically related, however, on cooling down the sample, the reverse transition VIII → II was not observed and an X-ray powder diffractogram corresponding to that of form VIII was collected (see SI), i.e. form VIII is a metastable form at room temperature.

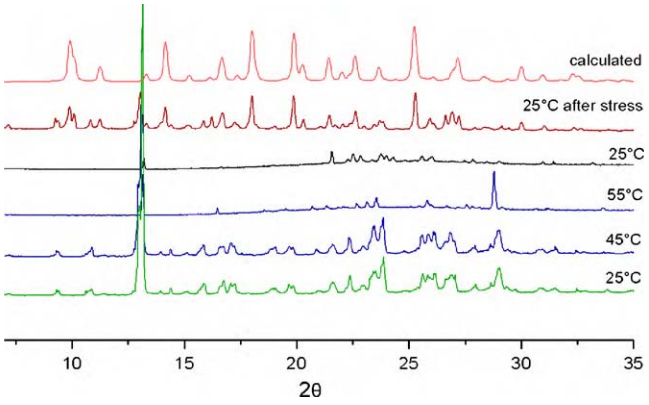


Fig. 8. VT-XRPD of physical mixture of acridine and vanillin.

Table 2
Physicochemical data for phemazine, acridine and vanillin.

Compound	Polymorph	Solid-to-solid phase transition, °C (±1 °C)	Melting point, °C (±1 °C)	ΔH, kJ mol^{-1} (±0.1 kJ mol^{-1})
Phenazine	α		174	23.5
	β		175	23.6
Acridine	II	101		2.2
	VIII		109	17.0
	III		106–109[a]	18.7
	IV		89	16.2
	V [37]			
	VI [39]		99 [39]	
	VII [39]		101 [39]	
Vanillin	I		82	22.4
	II		80	20.7

[a] DSC curves of form III (commercial product) always yielded lower temperature with respect to those obtained from DSC curves of form III re-crystallized, as expected.

Vanillin exists in four polymorphic forms [44], as detected by McCrone by hot-stage microscopy (HSM); until now, however, only the crystal structure of the thermodynamically stable form I had been reported [45], as well as the powder diffractogram of the metastable form II [46].

We found that spontaneous crystallization from the melt after complete melting yields two forms: form I, which grows as spherulites, and form III, which forms upon slow-growing as rectangular plates (according to McCrone). Both forms are visible in contact preparation method with both phenazine and acridine (see SI); however, we cannot exclude the presence of form II in the course of our HSM experiments, because also form II have the same spherulite morphology as form I. From polymorph screening of vanillin we obtained forms I and II (see Section 2 and SI).

4. Conclusions

Structures and methods of preparation of two new co-crystals of vanillin with phenazine and acridine are reported. The thermal behaviour and the relationship among the different forms of the reagents is also shown. It is interesting to note that, although vanillin is mainly produced by chemical synthesis [24], until now only two forms detected by Mc Crone have been reproduced in bulk, while form III has been observed only in a hot-stage experiment.

The products have been analyzed by DSC, HSM and (VT)XRPD. In both cases a eutectic melting point was detected and in the case of the acridine–vanillin system it is at 55 °C. The formation of co-crystal **2** is a liquid mediated reaction since it occurs only in the melt, while the co-crystal **1** phenazine/vanillin can be described as a true solid state reaction.

Acknowledgments

We acknowledge financial support from the University of Bologna and from MIUR (PRIN2006).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2010.04.021.

References

[1] P. Vishweshwar, J.A. McMahon, J.A. Bis, M.J. Zaworotko, J. Pharm. Sci. 95 (2006) 499.
[2] M.J. Zaworotko, Cryst. Growth Des. 7 (2007) 4.
[3] M.K. Stanton, A. Bak, Cryst. Growth Des. 8 (2008) 3856.
[4] T. Friscic, L.R. MacGillivray, Chem. Commun. (2009) 773.
[5] A.V. Trask, Mol. Pharm. 4 (2007) 301.
[6] S.L. Childs, M.J. Zaworotko, Cryst. Growth Des. 9 (2009) 4208.
[7] N. Schultheiss, A. Newman, Cryst. Growth Des. 9 (2009) 2950.
[8] I. Miroshnyk, S. Mirza, N. Sandlert, Expert Opin. Drug Deliv. 6 (2009) 333.
[9] J.A. Bis, P. Vishweshwar, D. Weyna, M.J. Zaworotko, Mol. Pharm. 4 (2007) 401.
[10] G.R. Desiraju, Angew. Chem., Int. Ed. Engl. 34 (1995) 2311.
[11] S. Mohamed, D.A. Tocher, M. Vickers, P.G. Karamertzanis, S.L. Price, Cryst. Growth Des. 9 (2009) 2881.
[12] C.B. Aakeroy, M.E. Fasulo, J. Desper, Mol. Pharm. 4 (2007) 317.
[13] S.L. Childs, G.P. Stahly, A. Park, Mol. Pharm. 4 (2007) 323.
[14] D. Braga, L. Maini, G. de Sanctis, K. Rubini, F. Grepioni, M.R. Chierotti, R. Gobetto, Chem. Eur. J. 9 (2003) 5538.
[15] M.R. Chierotti, R. Gobetto, Chem. Commun. (2008) 1621.
[16] R. Bolton, Rodd's Chem. Carbon Compd. 4 (2000) 173.
[17] L.S. Thomashow, D.M. Weller, R.F. Bonsall, L.S. Pierson III, Appl. Environ. Microbiol. 56 (1990) 908.
[18] M. Matthias, G.A. Ekta, V.M. Dmitri, B. Rolf, S.T. Linda, B. Wulf, ChemBioChem 10 (2009) 2295.
[19] B.D. Tilak, N.R. Ayyangar, Chem. Heterocycl. Compd. 9 (1973) 579.
[20] J. Keiser, J. Utzinger, Z. Premji, Y. Yamagata, B.H. Singer, Ann. Trop. Med. Parasitol. 96 (2002) 643.
[21] C. Korth, B.C.H. May, F.E. Cohen, S.B. Prusiner, Proc. Natl. Acad. Sci. U.S.A. 98 (2001) 9836.
[22] A. Barret, F. Tagliavini, G. Forloni, C. Bate, M. Salmona, L. Colombo, A. De Luigi, L. Limido, S. Suardi, G. Rossi, F. Auvre, K.T. Adjou, N. Sales, A. Williams, C. Lasmezas, J.P. Deslys, J. Virol. 77 (2003) 8462.
[23] L.S. Lerman, Proc. Natl. Acad. Sci. U.S.A. 49 (1963) 94.
[24] M.J.W. Dignum, J. Kerler, R. Verpoorte, Food Rev. Int. 17 (2001) 119.
[25] W. Hasenpusch, CLB Chem. Labor Biotech. 57 (2006) 458.
[26] K. Lirdprapamongkol, J. Svasti, H. Sakurai, I. Saiki, Beer Health Dis. Prev. (2009) e260.
[27] K. Lirdprapamongkol, H. Sakurai, N. Kawasaki, M.-K. Choo, Y. Saitoh, Y. Aozuka, P. Singhirunnusorn, S. Ruchirawat, J. Svasti, I. Saiki, Eur. J. Pharm. Sci. 25 (2005) 57.
[28] M. Polito, E. D'Oria, L. Maini, P.G. Karamertzanis, F. Grepioni, D. Braga, S.L. Price, CrystEngComm 10 (2008) 1848.
[29] T. Friscic, W. Jones, Cryst. Growth Des. 9 (2009) 1621.
[30] G.M. Sheldrick, *SHELXL97*, University of Göttingen, 1997.
[31] C.F. Macrae, P.R. Edgington, P. McCabe, E. Pidcock, G.P. Shields, R. Taylor, M. Towler, J. van De Streek, J. Appl. Crystallogr. 39 (2006) 453.
[32] A.L. Spek, Acta Crystallogr. A46 (1990) C34.
[33] W. Kraus, G. Nolze, Powder cell, ver. 3.2, 1999.
[34] N. Zencirci, T. Gelbrich, V. Kahlenberg, U.J. Griesser, Cryst. Growth Des. 9 (2009) 3444.
[35] K. Wozniak, B. Kariuki, W. Jones, Acta Crystallogr., Sect. C 47 (1991) 1113.
[36] W. Jankowski, M. Gdaniec, Acta Crystallogr., Sect. C 58 (2002) o181.
[37] F.H. Herbstein, G.M.J. Schmidt, Acta Crystallogr. 8 (1955) 399.
[38] L.B. McCusker, R.B.V. Dreele, D.E. Cox, D. Louër, P. Scardi, J. Appl. Crystallogr. 32 (1999) 36.
[39] X. Mei, C. Wolf, Cryst. Growth Des. 4 (2004) 1099.
[40] D.C. Phillips, F.R. Ahmed, W.H. Barnes, Acta Crystallogr. 13 (1960) 365.
[41] D. Phillips, Acta Crystallogr. 9 (1956) 237.
[42] R.D. Lowde, D.C. Phillips, R.G. Wood, Acta Crystallogr. 6 (1953) 553.
[43] Cambridge Structure Database, Cambridge Crystallographic Data Centre, UK, 2009.
[44] W. McCrone, Anal. Chem. 22 (1950) 500.
[45] R. Velavan, P. Sureshkumar, K. Sivakumar, S. Natarajan, Acta Crystallogr., Sect. C 51 (1995) 1131.
[46] K. Hussain, G. Thorsen, D. Malthe-Sørenssen, Chem. Eng. Sci. 56 (2001) 2295.