Novel 1,3-diethyl-2-thiobarbiturates of 2,2'-bipyridine and 1,10-phenanthroline: synthesis, crystal structure and thermal stability

Nicolay N. Golovnev[a], Maxim S. Molokeev[b,a,c*], Irina V. Sterkhova[d], Maxim K. Lesnikov[a],

[a] *Siberian Federal University, 79 Svobodny Ave., Krasnoyarsk 660041, Russia*
[b] *Laboratory of Crystal Physics, Kirensky Institute of Physics, Federal Research Center KSC SB RAS, bld. 38 Akademgorodok 50, Krasnoyarsk 660036, Russia*
[c] *Department of Physics, Far Eastern State Transport University, 47 Seryshev Str., Khabarovsk 680021, Russia*
[d] *Favorsky Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, 1 Favorsky, Irkutsk 664033, Russia*

[*] Corresponding author:
Maxim Molokeev
E-mail: msmolokeev@gmail.com
Laboratory of Crystal Physics, Kirensky Institute of Physics, Federal Research Center KSC SB RAS, bld. 38 Akademgorodok 50, Krasnoyarsk 660036, Russia
Tel.: +7-391-249-45-07

Abstract

The co-crystallization of 1,3-diethyl-2-thiobarbituric acid (HDetba) with 2,2'-bipyridine (Bipy) and 1,10-phenanthroline (Phen) in aqueous medium are prepared a salt co-crystal, BipyH(Detba)(HDetba) (**1**), and the salt, PhenH(Detba)·H_2O (**2**). The compounds have been characterized by single–crystal and powder X–ray diffraction, and TG-DSC. The nitrogen atoms of BipyH$^+$ adopt an *cis* conformation with the N—C—C—N torsion angle is −17.3(1)º. There are six intermolecular hydrogen bonds O—H···O, N—H···O, C—H···O and C—H···S in (**1**) which form 2D plane network. The Detba$^−$ ion and HDetba molecule form pair by means of hydrogen bonds. The Detba$^−$ anions in (**2**) do not form dimers, they are connected by N—H···O, C—H···S and C—H···O hydrogen bonds only with PhenH$^+$ cations and water molecules which form 3D net. The different π–π interactions between the rings are found in the (**1**)-(**2**). The compounds are characterized by powder XRD, TG-DSC.

Keywords: 1,3-diethyl-2-thiobarbituric acid; 1,10-phenanthroline; 2,2'-bipyride; ; salt; salt co-crystal; X-ray diffraction; infrared spectroscopy; thermal stability

1. Introduction

Derivatives of barbituric acid have anesthetic, sedative, anticonvulsive, antimicrobial, antifungal, antiviral and anti-cancer properties [1, 2]. Moreover, the organic salts of barbituric

acids and their metal complexes possess potentially useful properties, for instance, biological activities [3, 4], solvatochromism, molecular recognition, photoluminescence, catalytic activity etc. [2]. They are promising materials of nonlinear optics (NLO) [5, 6] and organic solar cells [7]. The structures of metal complexes with barbituric (H_2ba) and 2-thiobarbituric acids (H_2tba) and some of their derivatives have been mainly studied [8, 9]. Organic salts and co-crystalls of barbituric acids are less studied, for example, there are no structural data on the compounds of 1,3-diethyl-2-thiobarbituric acid ($C_8H_{12}N_2O_2S$, HDetba) (Fig. 1), although it and its compounds can find practical application. For example, HDetba is proposed as an alternative to acidic photopolymerizable dental materials [10] and for determining nicotine and twelve metabolites in human urine and animals using high-performance liquid chromatography [11]. Its compounds can be used as NLO materials [12] and for the manufacture of field-effect transistors [13]. Like the H_2tba, HDetba has five potential hydrogen bonding acceptors: (i) two carbonyl O atoms, (ii) one S atom and (iii) two N atoms. Each of the two N atoms is linked to one -C2H5 group and therefore can only act as a weak hydrogen bonding acceptor. In the absence of the strong hydrogen bonding donors in HDetba, they can be replaced by C atoms, forming the weak C—H···Y hydrogen bonds (Y = F, O, N) [14]. Therefore, further exploration of organic systems of 1,3-diethyl-2-thiobarbituric acid can provide abundant supramolecular architectures.

The free bases of 2,2'-bipyridine (Bipy) and 1,10-phenanthroline (Phen) are used as the complexing agents for iron and other metal ions in chemical and biological systems. A classical use of Phen is that of the Fe(II)-complex (ferroin) as an indicator in redox titrations [15]. Bipy is a very interesting ligand because of its potential application in the preparation of nonlinear optical materials (NLO), sensor objects, coatings and catalysis [16], single-molecule magnets [17]. As a part of our continuing investigations on structures and properties of 1,3-diethyl-2-thiobarbiturate compounds [18-26], in the present report a salt co-crystal 2,2'-bipyridin-1-ium 1,3-diethyl-2-thiobarbiturate1,3-diethyl-2-thiobarbituric acid, BipyH(Detba)(HDetba) (**1**), and a salt phenanthrolin-1-ium 1,3-diethyl-2-thiobarbiturate monohydrate, PhenH(Detba) · H_2O (**2**), were synthesized and characterized by single-crystal and powder X-ray diffraction methods. Also thermal decomposition of compounds was studied. Thermal decomposition of compounds was also studied. Any information on the structure of the solid and the properties of Bipy or Phen compounds with HDetba is not found in the scientific literature [9].

2. Experimental section

2.1. Reagents and synthesis

1,3-diethyl-2-thiobarbituric acid, 1,10-phenanthrolinium chloride monohydrate and 2,2'-bipyridine were purchased from Sigma-Aldrich and used without further purification. Sodium

hydroxide and ethanol (95%, CAS 64-17-5) as a reagents analytical grade (Acros) were used without additional purification.

Compound BipyH(Detba)(HDetba) (**1**) was prepared by the crystallization from the ethanol. 2,2'-bipyridine (0.039 g, 2.5 mmol) and 1,3-diethyl-2-thiobarbituric acid (0.1 g, 5.0 mmol) were dissolved in ethanol (1.5 cm^3) at room temperature. A light yellow transparent solution was left at a temperature of 3 °C. After 2 days, the formation of yellow rhombic single crystals was observed. The crystalline product was filtered off and dried between sheets of filter paper in air at room temperature (yield 67%). The single crystals suitable for structural analysis were selected directly from the total mass of precipitate (**1**). The elemental analysis for $C_{26}H_{32}N_6O_4S_2$ (**1**): Calc.: C, 56.1%; H, 5.79%; N, 15.1%; S, 11.5%. Found: C, 56.7%; H, 5.58%; N, 14.9%; S, 11.2%. Also compound (**1**) was crystallizes from the aqueous solution at pH = 3.1 (a multitest IPL-103 pH meter, Semico, Russia) with yield 40-60%. The repeated experiments showed poor reproducibility of this method.

The salt, PhenH(Detba)·H$_2$O (**2**), was crystallized from the water. 1,10-phenanthroline hydrochloride monohydrate (0.117 g, 5.0 mmol)) was dissolved in 5 ml of water and then an equimolar amount of solid NaOH was added. A white precipitate of Phen was formed. Then to this mixture the 1,3-diethyl-2-thiobarbituric acid (0.1 g , 5.0 mmol) was added. The sediment partially dissolved, changing color from white to yellow. The mixture was heated to 80 °C and kept at this temperature for one hour until the yellow precipitate dissolves completely. The light yellow solution was slowly cooled and allowed to evaporate at room temperature (pH = 3.9). A week later, a little amount of orange oil was formed in the solution, the amount of which was increased as the water evaporated. The solid residue after complete removal of water was a mixture of orange crystals and a glassy substance. The orange single crystals of (**2**) were taken directly from the resulting mixture. Several these single crystals are used for the structural analysis and thermal measurements. However, we could not get compound (**2**) at a volume sufficient for powder XRD measurements. The attempts to obtain other compounds of HDetba with Bipy and Phen by the crystallization from an aqueous solution were unsuccessful.

2.2. X-ray diffraction analysis

The intensity patterns were collected from single crystals (**1**) and (**2**) at 100 K using the D8 Venture X-ray single crystal diffractometer (Bruker AXS) equipped with a CCD-detector, graphite monochromator and a Mo Kα radiation source. The absorption corrections were applied using the SADABS program. The structures were solved by the direct methods using package SHELXS and refined in the anisotropic approach for non-hydrogen atoms using the SHELXL program [27]. All hydrogen atoms were found *via* Fourier difference maps. Further, the

hydrogen atoms, which are linked with C, N atoms in the HDetba molecule, Detba$^-$, BipyH$^+$, PhenH$^+$ ions in **1**, **2** were positioned geometrically as riding on their parent atoms with d(C—H) = 0.93−0.98 Å, d(N—H) = 0.86−0.89 Å depending on geometry and U$_{iso}$(H) = 1.2U$_{eq}$(C, N). All hydrogen atoms of the H$_2$O molecules were refined with bond length restraint d(O—H) = 0.9 Å and U$_{iso}$(H) = 1.2U$_{eq}$(O). The structure test for the presence of missing symmetry elements and possible voids was produced using the PLATON program [28]. The DIAMOND program is used for the crystal structure plotting [29].

Powder X-ray diffraction data of (**1**) was obtained using diffractometer D8 ADVANCE (Bruker) equipped by a VANTEC detector with a Ni filter. The measurements were made using Cu Kα radiation. The structural parameters defined by a single crystal analysis were used as a base in the powder pattern Rietveld refinement. The refinement was produced using program TOPAS 4.2 [30]. The low *R*-factor and the good refinement results (Table 1S, Fig. 1S) indicate the phase purity of the powder sample (**1**).

2.3. Physical measurements

TGA was carried out on the simultaneous SDT-Q600 thermal analyzer (TA Instruments, USA) under the dynamic air atmosphere (50 ml/min flow rate) within 25–350 °C at the scan rate of 10 °C/min. The compound weight was 4.516 mg for (**1**) and 4.590 mg for (**2**). Platinum crucibles with perforated lids were used as the containers. The IR absorption spectra of the compounds inserted into the KBr tablets were recorded over the range of 400–4000 cm^{-1} at room temperature on an FT-IR spectrometer Nicolet 6700 (Thermo Scientific, USA, SFU CEJU).

3. Results and discussion

3.1. Theoretical consideration

2,2'-bipyridine and 1,10-phenanthroline behave as weak bases, often forming monoprotonated species of BipyH$^+$ and PhenH$^+$, respectively, as a result of protonation of one N atom. In aqueous solution the stepwise acidity constants are pK$_{a1}$ = 1.51, pK$_{a2}$ = 4.48 for the BipyH$_2$$^{2+}$, and pK$_{a1}$ = 1.92, pK$_{a2}$ = 5.01 for the PhenH$_2$$^{2+}$ (30 ºC, 0.1M KNO$_3$) [31]. The acidity constant is pK$_{a1}$ = 2.78 for HDetba (25 ºC, 0.25M KCl) [32]. The HDetba speciation (Fig. 2) shows the predominance of an anionic species at pH > 4 (α`$_1$ ≈ 1), and a neutral species at pH < 1.5 ($\alpha$`$_2$ ≈ 1) in aqueous solution. The neutral molecule Bipy species (Fig. 2) is dominated at pH > 6 (α_0 ≈ 1), a cationic species BipyH$^+$ between pH 2 and pH 4 (α_1 ≈ 0.7−0.8). A diprotonated cationic species BipyH$_2$$^{2+}$ (α_2) forms already at pH < 3, and it is dominated at pH < 1. The speciation of Phen − HDetba system (Fig. 2S) shows the predominance of a neutral Phen species

at pH > 6.5, a cationic species PhenH$^+$ between pH 2.5 and pH 4.5, and a cationic species PhenH$_2^{2+}$ at pH < 1. According to the species distribution diagrams, pH values of aqueous solution were chosen for synthesis (**1**) [pH ≈ 3] and (**2**) [pH ≈ 4].

It is generally accepted that the reaction of an acid with the base is expected to form a salt if ΔpK$_a$= pK$_a$(base) − pK$_a$(acid) > 2 or 3 [33]. Indeed, when the equimolar amounts of HDetba interact with Phen (ΔpK$_a$ = 2.23), salt (**2**) was obtained. The difference in the values of K$_a$ of BipyH$^+$ и HDetba is less (ΔpK$_a$ = 1.70), which promoted the formation of (**1**) salt co-crystals at pH 3.

3.1. Crystal structures of (1)

The unit cells of (**1**) correspond to the triclinic symmetry. Space group *P*-1 was determined from the statistical analysis of the reflection intensities. The main crystal data are enumerated in Table 1. The compound (1) is a salt co-crystal [34]. The independent part of the unit cell contains one BipyH$^+$ ion, one Detba$^-$ ion and one HDetba molecule (Fig. 3a). The main bond lengths C—N, C—C and valence angles (Table 2S) practically coincide with those found earlier in other related compounds of HDetba [18−26], but C—S and O1—C4 bonds are slightly (0.01-0.02 Å) shorter. However, the O2A—C6A bond is noticeably (0.03–0.04 Å) longer than the others (Table 2S), since the O2A atom in the HDetba molecule is bonded to the hydrogen atom, that is, the HDetba acid is in the enol form. The conformations of Bipy and its protonated species constitute an important aspect in the understanding of the properties of this popular ligand in coordination chemistry. Bipy exists in a *trans* conformation in the solid state [35]. The *cis* conformer of the cation is by far the most stable than *trans*, according to *ab initio* self consistent-field (SCF) calculation [36]. As expected, 2,2'-bipyridine offers interesting motifs by virtue of the predominantly *cis* dispositions of the pairs of nitrogen atoms in its monoprotonated salts [8]. The monoprotonated *cis* species of BipyH$^+$ could be stabilized by a cationic hydrogen bond N—H···N, as in numerous proton sponges [14]. However, there are also compounds in which BipyH$^+$ is in the form of a *trans* conformer [8, 37]. In (**1**), the bipyridinium cation has a *cis* conformation and the N—C—C—N torsion angle is −17.3(1)º. It clearly indicates that BipyH$^+$ does not behave as a proton sponge. As expected [38], an weak intramolecular hydrogen bond is found in the BipyH$^+$ cation with an N2···N1 distance of 2.654(1) Å and N2—H···N1 angle of 106.52(7)º. The main bond lengths C—N, C—C and the angles in the BipyH$^+$ practically coincide with those found earlier in other related compounds [8]. For instance, the bond lengths C7C—C8C (1.4790(16) Å), N1C—C8C 1.3470(15) Å) and N2C—C7C (1.3514(16) Å) coincide with those found in [BipyH]ClO$_4$ [C7C—C8C (1.481 Å), N1C—C8C 1.347 Å) and N2C—C7C (1.352 Å)] (CSD refcode PYPYPC02) [39]. In (**1**), the BipyH$^+$ ion is a planar, the standard

deviation of atoms from this plane is 0.183 Å. As expected [40], the effect of protonation at the N2 site in BipyH$^+$, is manifested in the C—N—C angles being much wider than those at the unprotonated N1 atom [123.4(1)° *versus* 117.2(1)°]. There are six intermolecular hydrogen bonds O—H···O, N—H···O, C—H···O and C—H···S in the structure (Table 2) which form 2D plane network with the supramolecular motifs R$_2^1$(6), R$_2^1$(7) and R$_8^8$(39) (Figure 4a). The one Detba$^-$ ion and one HDetba molecule join to form pairs by means of O2A—H1A···O2B and C5A—H5A···O2B hydrogen bonds. In the salt co-crystal (**1**), a strong hydrogen bond O2A—H1A···O2B is characterized by a small distance d(O···O) = 2.440 (1) Å, a large value of the angle O2A—H1A···O2B (178(2) °) and a long bond O2A—H1A (d(O2A—H1A) = 1.32(2) Å). The close geometric parameters of the hydrogen bond O—H···O were previously established in the salt co-crystal of the piperidine (Pipe) with 2-thiobarbituric acid, PipeH(Htba)(H$_2$tba) (**3**) [41]. In the formation of strong hydrogen bonds, the increase in the distance d(O—H) reaches 0.2Å [42] as in compound (**1**). In (**3**), the Htba$^-$ ion and the H$_2$tba molecule also form a pair, but due to two hydrogen bonds N—H···O. These pairs are combined by the intermolecular hydrogen bonds O—H···O and N—H···O into infinite chains. Replacing the hydrogen atoms of the NH groups in H$_2$tba by the C$_2$H$_5$ groups leads to a weakening of the N atoms donor capacity. In this case, weak C—H···O hydrogen-bonds in (**1**) play an important role in the formation of the supramolecular structure. The C—H···O hydrogen-bond distances in (**1**) are of the same order of magnitude as those reported previously [37].

Topological analysis of the net, using simplification and excluding all 0-, 1- and 2-coordinated nodes revealed that this is uninodal 4-c net with point symbol (4^3.6^3) which is known as **SP (6,3)Ia** [30]. It should be noted that H-bond net of NH$_4$Detba [18] form relative 2D net with point symbol (4^4.6^2) named **sql**. The compounds LiDetba and NaDetba [19] have relative 2D nets (4^2.6^4) named **SP (6,3)Id**. The compounds M(Detba)$_2$(H$_2$O)$_2$ (M = Ca, Sr, Mn) [23, 26] also have 2D nets (4^4.6^2) **sql**, the compound Eu(Detba)$_3$ [24] has 2D net (6^3) **hcb**, and Pb(Detba)$_2$ [21] has 2D net (4^3)$_2$(4^4.6^6.8^3) **kgd**. The common of all these nets is that they form only 2D nets and this can be associated with small amount hydrogen bond donors in HDetba ligands. Further analysis of interactions in (**1**) revealed π−π interactions between HDetba, Detba$^-$ and BipyH$^+$ rings (Table 3S, Fig. 3Sa).

3.2. Crystal structures of (2)

The unit cell of (**2**) also corresponds to triclinic symmetry. The main crystal data are shown in Table 1. The independent part of the unit cell contains two Detba$^-$ ions, two PhenH$^+$ ions and two water molecules. (Fig. 3b). The structure test for the presence of missing symmetry elements revealed nonspacegroup translation A (0, 1/2, 1/2). As far as groups of atoms (O1C, O1D);

(C9C, C9D); (O1W, O2W) violated this translation so the crystal has pseudosymmetry and no obvious spacegroup change needed. The main bond lengths C—N, C—C (Table 2S) and the valence angles in HDetba⁻ ion coincide with those found earlier in other related compounds [18−26] and like in (**1**) C—S and O1—C4 bonds are slightly (0.01−0.02 Å) shorter. Also in PhenH⁺, the C1A—C2A (1.434(2) Å), C1B—C2B 1.436(2) Å), N1A—C2A (1.363(2) Å), N1B—C2B (1.363(2) Å), N2A—C1A (1.357(2) Å), and N2B—C1B (1.359(2) Å) distances are coincided with those found earlier (CSD refcode CUZDIK) [43]. PhenH⁺ ions are practically flat, so the standard deviation of atoms from planes for ions A and B is only 0.048 and 0.052 Å, respectively. As in compound (**1**), the effect of protonation at the N2A and N2B sites in A and B respectively, is manifested in the C—N—C angles being much wider than those at the unprotonated nitrogen atoms [123.1(1), 123.0(1)° *versus* 116.5(1), 116.4(1)°]. Just like in (**1**), a weak intramolecular hydrogen bond is found in A and B of PhenH⁺ cation with an N2···N1 distance of 2.7476(2) Å and 2.7517(2) Å, and N—H···N angle of 104.121(9)°, 104.31(1)°, respectively. The torsion angle C8—C7—C9—C10 of Detba⁻ ions in (**1**)−(**2**) are small (<4 deg) therefore the Detba- ions present in conformational state (A). The torsion angle C8–C7–C9–C10 for Detba⁻ ions in (**1**)-(**2**) is small (<4 deg) therefore Detba ions are represented only a conformer (A) [18].

There are nine intermolecular hydrogen bonds N—H···O, O—H···O, C—H···O and C—H···S, in the structure (Table 2) which form 3D net. Some 2D nets can be marked (Fig. 4b) and the shortest ring motifs in them are $R_4^4(18)$, $R_4^4(20)$, $R_6^6(20)$. The water molecules participate in moderately strong O—H···O interaction with anions (d(O···O) = 2.809 and 2.876 Å). Also, there are π−π interactions between Detba⁻ and PhenH⁺ rings (Table 3S, Fig. 3Sb). The self-assembly, and crystal structure for 1,10-phenanthrolinium barbiturate monohydrate, PhenH(Hba)·H₂O (CSD refcode MUYVET), and 1,10-phenanthrolinium 2-thiobarbiturate, PhenH(Htba) (CSD refcode MUYVET), are reported earlier [5]. In them two barbiturate or thiobarbiturate moieties join to form dimers by means of N—H···O hydrogen bonds (2.805 and 2.823 Å). These dimers are stabilized by the cation−anion interactions of N—H···O and N—H···N types. As in (**2**), the water molecules in PhenH(Hba)·H₂O participate in the formation of moderately strong hydrogen bonds with Hba⁻ anions. Just like in (**1**)-(**2**), in PhenH(Hba)·H₂O and PhenH(Htba) the C—N—C angles for protonated N atoms больше чем at the unprotonated N atoms, and the charge in O1=C4—C5—C6=O2 group of Hba⁻ and Htba⁻ is delocalized.

Topological analysis of (**2**) using ToposPro program [30] showed that this 3D net is 6-nodal (3-c)(4-c)(4-c)(5-c)(5-c)(5-c) net with point symbol $(3.4.5.6^3)(3.4.6^5.7^2.8)(3.4^2.5.6^2)(4.6.8)(4^2.6^5.7^2.8)(4^3.6^6.7)$ which is new.

3.4. Thermal decomposition

The TG-DSC curves of BipyH(Detba) (**1**) and(PhenH(Detba)·H_2O (**2**) at 25-300 °C are shown in Fig. 4S and Fig. 5S, respectively. The TG curve clearly indicated that thermal decomposition/oxidation of (**1**) occurs in one step (Fig. 4S). An endothermic effect for (**1**) at 110.3 °C corresponds to the compound melting. This value of melting point is higher than for Bipy (70.5 °C) and less than for HDetba (112°C, [19]), that confirms the individuality of the compound (**1**). The decrease in the mass of the substance at T > 112 °C corresponds to the oxidation of compound and evaporation of HDetba and Bipy. In the range of 150−230 °C, the mass of the sample decreased rapidly in accordance to the mean TG curve (Fig. 4S). The transformations at 150−230 °C are accompanied by the exo effect at ~160 °C and endo effect at 216 °C. The appearance of a weak endothermic peak at 216 °C can be explained by the thermal effects superposition of oxidative decomposition and evaporation of thermolysis products. In the temperature range of 150−230 °C, almost all the bipyridine is removed, which is confirmed by the absence of an endothermic effect at the boiling point of Bipy (273 °C). At 250 °C, the total mass loss reaches ~95%, and then the mass decreases only by ~ 1% when heated to 300 °C. The carbonaceous residue (~5%) is probably formed as a result of incomplete oxidation of the HDetba molecules and Detba⁻ ions with the release of CO_2. As seen from the TG curve (Fig. 5S), the thermal decomposition process for the (**2**) can be divided into three stages. The first stage starts in the range of 70—135 °C with mass loss of 4.60%, which corresponds to the loss of H_2O molecule with the theoretical mass loss of 4.52%. The Phen and HDetba have melting point of 117 °C and 112 °C [19], respectively, these data confirm the individuality of the compound (**2**). The dehydration of (**2**) is accompanied by endo effect at 93.6 °C. In the second stage of transformation at 140–250 °C, evaporation and oxidation of 1,3-diethyl-2-thiobarbituric acid and phenanthroline occur simultaneously. In the third stage, above 250 °C, the endothermic evaporation processes of HDetba and Phen are likely to become increasingly important, as evidenced by the endothermic peak at 275 °C on the DSC curve. The thermolysis final product of (**2**) at 310 °C consists predominantly of liquid Phen, that agrees with its boiling point (300 °C).

4. Conclusions

For the first time, the organic salt co-crystal (**1**) and salt (**2**) of 1,3-dialkyl-2-thiobarbituric acid are prepared and structurally characterized. The compounds were obtained by reaction in an aqueous medium of an acid with the Bipy and Phen. At a Bipy : HDetba = 1: 2 molar ratio, an anhydrous salt co-crystal (**1**) forms containing in the formula unit one monoprotonated 2,2-bipyridine, one deprotonated acid anion, Detba⁻, and neutral acid, HDetba. The salt (**2**) was obtained by reaction of an acid with the 1,10-phenanthroline at a Phen : HDetba = 1 : 1 molar ratio. It contains one PhenH⁺ cation, one Detba⁻ anion and one water molecule. Образование солевого со-кристалла (**1**) и соли (**2**) согласуется с "ΔpK$_a$ rule" предложенным ранее для двухкомпонентных органических кристаллов[33].

The protonation of the N atom in (**1**) and (**2**) results in a slight deformation of the ring and consequently a slightly larger C—N—C bond angle (>120°). In (**1**), the O—H···O and C—H···O intermolecular hydrogen bonds connect the anion and neutral acid in pair. The O—H···O hydrogen bond between an acid (HDetba) and its conjugate base (Detba⁻) is very strong with d(O···O) = 2.440(1) Å. The Detba⁻ anion is bound to one BipyH⁺ ion by two N—H···O and C—H···O intermolecular hydrogen bonds (Fig. 4a). HDetba is bound by two C—H···O intermolecular hydrogen bonds with one BipyH⁺ cation and C—H···S intermolecular hydrogen bond with another. BipyH⁺ cations in (**1**), as well as PhenH⁺ in (**2**), are not directly connected to each other (Fig. 2). The Detba⁻ anions in (**2**) do not form dimers, unlike barbiturate and thiobarbiturate ions in the corresponding phenanthrolinium salts [5]. Each chain of two water molecules is bound by hydrogen bonds OW—HW···O with three Detba⁻ anions, which in turn are connected with to the PhenH⁺ cations by the N—H···O, C—H···S hydrogen bonds. The C—H···X (X = O, S) weak hydrogen bonds exert a significant influence on the supramolecular architecture of the compounds. The compound (**2**) has a new topology of 3D net.

Several types of π–π interactions between the rings are found in the (**1**)-(**2**) (Fig. 2S). Co-crystal of (**1**) melts at 110.3 ° C and salt (**2**) is dehydrated in the range of 70-135 ° C, a further increase in temperature leads to their oxidative decomposition.

Supplementary data

The crystallographic data (excluding structure factors) for the structural analysis have been deposited with Cambridge Crystallographic Data Centre ((**1**) - CCDC # ????; (**2**) - CCDC # ????). The information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk, or www: www.ccdc.cam.ac.uk).

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References

1. Bondock, S. Tarhoni A. E.,. Fadda A. A. //Phosphorus Sulfur Silicon Relat. Elem. - 2007. - Vol. 182. - P. 1915 – 1936.

2. Mahmudov, K. T. Barbituric acids as a useful tool for the construction of coordination and supramolecular compounds / K. T. Mahmudov, M. N. Kopylovich, A. M. Maharramov et al. //Coord. Chem. Rev. – 2014. – Vol. 265. – P. 1-37.

3. El-Gahani, M. A. Reactivity of five-coordinate Co(II), Ni(II) and Cu(II) chelates towards thiobarbituric acid as a sulfur donor ligand and their antimicrobial activities / M. A. El-Gahani, Ibrahim S.A., H. M. A. Salman // Synth. React. Inorg. Met.-Org. Chem. - 1991. - Vol. 21., N 10. - P. 1497–1509.

4. Balas V. I. Synthesis, structural characterization and biological studies of the triphenyltin (IV) complex with 2-thiobarbituric acid / V. I. Balas, I. I. Verginadi, G. D Geromichalos et al.//Eur. J. Med. Chem. – 2011. – Vol. 46. – №. 7. – P. 2835-2844.

5. Ivanova B.B., Spiteller M. Cryst. Growth Des. 2010, V.10. P.2470-2474.

6. Pan, Z.R.Synthesis, structure and nonlinear optical properties of three dimensional compounds / Z. R. Pan, Y. C. Zhang, Y. L. Song et al.// J. Coord. Chem. - 2008. - Vol. 61, N. 20. - P. 3189–3199

7. Gryl M. Acta Cryst. 2015. B71. P. 392-405.

8. Cambridge Structural Database. Cambridge (UK): Univ. of Cambridge, 2017.

9. Головнев Н.Н., Молокеев М.С. 2-тиобарбитуровая кислота и ее комплексы с металлами: синтез, структура и свойства. Красноярск: Сиб. федер. ун-т, 2014. 252 с.

10. Munchow E., Valente L.L. Peralta S.L., Fernandez M.R., Lima G.S., Petzhold C.L., Piva E., Ogliari F.A. //J. Biomed. Mater. Res. B. 2013 doi: 10.1002/jbm.b.32933]

11. Rustemeier K., Demetriou D., Schepers G., Voncken P. // J. Chromatogr. 613 (1993) 95-103.

12. Domagalska B.W., Wilk K.A., Szymusiak H., Zielinski R. // Computers Chem. 24 (2000 359-367.

13. Sni Y., Mikosch A., Winzenberg K.N., Kemppinen P., Easton C.D., Bilic A., Forsyth C.M., Dunn C.J., Singh Th.B.,Collis G.E.// J. Mater. Chem. C. 2014. 2. 3895-3899.

14. [Steed].

15. Braun D.E., Raabe K., Schneeberger A., Kahlenberg V., GriesserU.J. Molecules. 2017. 22. 2238-2257].

16. Z.-X. Chang , Li Y., Li K.-C., Song W.-D, Li Q.-S. // Inorg. Chem. Commun. 2007. 10. N 11. P.1276-1280.

17. H. L.C. Feltham, S. Brooker. // Coord. Chem. Rev. 276 (2014) 1–33.

18. Molokeev M.S., Golovnev N.N., Vereshchagin S.N., Atuchin V.V. // Polyhedron. 2015. V. 98. P. 113-119.

19. Golovnev N.N., Molokeev M.S., Vereshchagin S.N., Sterkhova I. V., Atuchin V.V. // Polyhedron. 2015. V. 85. P. 493-498.

20. Golovnev. N.N., Molokeev M.S., Lutoshkin M.A. // Russ. J. Inorg. Chem. 2015. V. 60. № 5. P. 572. Ag

21. Golovnev N.N., Molokeev M.S. Golovneva I.I. //Russ. J. Coord. Chem. 2015. V. 41. № 5. P. 300-304. Pb

22. Golovnev, N.N., M.S. Molokeev, M.K. Lesnikov, Atuchin V. V. // Chem. Phys. Lett. – 2016. – Vol. 653. – P. 54-59. [M $(H_2O)_6$](1,3-diethyl-2-thiobarbiturate)$_2$·2H$_2$O

23. Golovnev, N. N., M. S. Molokeev, A. S. Samoilo, Atuchin V.V. / J. Coord. Chem. – 2016. – Vol. 69, N 6. – C. 957-965. M(H_2O)$_2$(1, 3-diethyl-2-thiobarbiturate)$_2$ M= Ca^{2+}, Sr^{2+}

24. Golovnev, N. N., M. S. Molokeev, S. N. Vereshchagin // Russ. J. Coord. Chem. – 2016. – Vol. 57, N 1. – P. 167-174. europium (III)

25 Golovnev N. N., Molokeev M. S., Smolentsev A. I., Lesnikov M. K. // Russ. J. Coord. Chem. 2017. V. 43. № 2. P. 82-85. Co$_2$(Bu)$_4$(Hdetba)$_2$

26. Golovnev N. N., Molokeev M. S., Sterkhova I. V., Lesnikov M. K., Atuchin V. V. // Polyhedron. 2017. V. 134. P. 120-125. Mn

27. [SHELX]. G.M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112–122.

28. [PLATON]. PLATON – A Multipurpose Crystallographic Tool. Utrecht University, Utrecht, The Netherlands, 2008.

29. [DIAMOND]. K. Brandenburg, M. Berndt, DIAMOND - Visual Crystal Structure Information System CRYSTAL IMPACT, Postfach 1251, D-53002 Bonn

30. [TOPAS]. Bruker AXS TOPAS V4: General profile and structure analysis software for powder diffraction data. – User's Manual, Bruker AXS, Karlsruhe, Germany, 2008.

31. Sharkar M., Kam K., Reddy M. // Indian. J. Chem. 1989, 28A, 437.

32. Lutoshkin M. A., Petrov A.I., Golovnev N. N. // J. Solution Chem. 2016. V. 45. N 10. P. 1453-1467.

33. S. L. Childs, P. Stahly, A. Park, *Mol. Pharmaceutics*, **2007**, *4(3)*, 323.

34. Cherukuvada, R. Kaur, T. N. G. Row, *CrystEngComm.*, **2016**. DOI: 10.1039/c6ce1835a].

35. F.E. Kuḥn, M. Groarke, E. Bencze, E. Herdtweck, A. Prazeres, A.M. Santos, M.J. Calhorda, C.C. Roma, I.S. GonÁalves, A.D. Lopes, M. Pillinger. Chem. Eur. J. 2002, 8, No.10. P. 2370-2383.

36. Howard, S. T. J. Am. Chem. Soc. 1996. 118 (42), 10269-10274

37. Ma G., Ilyukhin A., Glaser J. Cryst. Struct. 2000. C56. 1473-1475

38. An B., Bay Y., Yang F.Z. // Z. Naturforsch. 2012. 67B. 85-88.

39. Kadarkaraisamy M., Engelhart D.P., Basa P.N., Sykes A.G. // J. Coord. Chem. 2010. 63(13) 2261-2267

40. R.D. Gillard, M. B. Hursthouse, K.M. A. Malik, S. Paisey J. Chem. Cryst. V.28, No.8, 1998. p. 611-618

41. Головнев Н. Н., Молокеев М. С., Стерхова И.В., Головнева И.И.. Структура ионных со-кристаллов 2-тиобарбитурат пиперидиния –2-тиобарбитуровая кислота // Журнал 42. структурной химии. 2016. Т. 57. № 6. С. 1308–1311.

42. Vishweshwar P., Nangia A., Lynch. V.M. // Chem. Commun. – 2001. – P.179-180 DOI: 10.1039/b007346f]

43. Hensen K., Spangenberg B., Bolte M. Cryst. Struct. 2000. C56. 208-210.

44. Athimoolam S., Natarajan S. (2007). Acta Cryst. C63, o263-o266.

Graphical Abstract

Table 1. Crystal structure parameters of (**1**) and (**2**)

Single crystal	BipyH(Detba)(HDetba) (**1**)	PhenH(Detba)·H_2O (**2**)
Moiety formula	$C_{26}H_{32}N_6O_4S_2$	$C_{20}H_{22}N_4O_3S$
Dimension (mm)	0.40×0.31×0.18	0.34×0.31×0.15
Color	Yellow	Yellow
Molecular weight	556.69	398.48
Temperature (K)	100	100
Space group, Z	P-1, 2	P-1, 4
a (Å)	10.1936 (6)	10.9194 (9)
b (Å)	11.0122 (6)	13.351 (1)
c (Å)	13.4505 (8)	13.8901 (11)
α (º)	68.875 (2)	104.723 (3)
β (º)	87.388 (2)	101.020 (3)
γ (º)	72.767 (2)	99.626 (3)
V (Å^3)	1342.00 (14)	1872.1 (3)
ρ_{calc} (g/cm^3)	1.378	1.414
μ (mm^{-1})	0.243	0.203
Reflections measured	57298	90030
Reflections independent	7863	10998
Reflections with F > 4$\sigma(F)$	6564	7730
$2\theta_{max}$ (°)	60.15	60.16
h, k, l - limits	-14 ≤ h ≤ 14; -15 ≤ k ≤ 15; -18 ≤ l ≤ 18	-15 ≤ h ≤ 15; -18 ≤ k ≤ 19; -19 ≤ l ≤ 19
R_{int}	0.0381	0.0775
The weighed refinement of F^2	w=1/[$\sigma^2(F_o^2)$+(0.0385P)^2+0.6513P]	w=1/[$\sigma^2(F_o^2)$+(0.056P)^2+0.744P]
Number of refinement parameters	350	521
$R1$ [F_o > 4$\sigma(F_o)$]	0.0344	0.0493
$wR2$	0.0891	0.1241
$Goof$	1.017	1.036
$\Delta\rho_{max}$ (e/Å^3)	0.382	0.893
$\Delta\rho_{min}$ (e/Å^3)	-0.359	-0.406
$(\Delta/\sigma)_{max}$	0.001	0.404

Table 2. Hydrogen-bond geometry in (**1**) and (**2**) structures (Å, °).

| D—H	d(D—H)	d(H⋯A)	∠ D—H⋯A	D⋯A	A	Transformation for A atom
BipyH(Detba)(HDetba) (**1**)						
N2C—H2C	0.86	1.91	142	2.6395 (14)	O1B	x, y, z
C6C—H6C	0.93	2.39	163	3.2923 (17)	O1A	x, y, 1+z
C9C—H9B	0.93	2.53	168	3.4411 (15)	O1A	x, y, 1+z
C4C—H4C	0.93	2.76	171	3.6822 (14)	S1	1+x, -1+y, 1+z
C5A—H5A	0.93	2.6486(7)	121.47 (8)	3.233 (1)	O2B	x, y, z
O2A—H1A	1.12(2)	1.32 (2)	178 (2)	2.440 (1)	O2B	x, y, z
PhenH(Detba)·H₂O (**2**)						
N1A—H1A	0.86	1.94	142	2.671 (2)	O2D	x, y, z
N1B—H1B	0.86	1.96	139	2.674 (2)	O2C	x, y, z
O1W—H1WA	0.90 (2)	1.94 (2)	163 (2)	2.809 (2)	O2C	x, y, z
O1W—H1WB	0.83 (2)	2.11 (2)	154 (2)	2.876 (2)	O1D	1-x, 1-y, 1-z
O2W—H2WA	1.05 (2)	1.82 (2)	168 (2)	2.854 (2)	O1W	x, y, z
O2W—H2WB	1.05 (2)	1.79 (2)	170 (2)	2.827 (2)	O2D	x, y, z
C12B—H12B	0.93	2.20	142	2.992 (2)	O1C	1-x, 2-y, 2-z
C10A—H10A	0.93	2.84	145	3.639 (2)	S2	x, 1+y, z
C12A—H12A	0.93	2.39	126	3.030 (2)	O1D	1-x, 1-y, 1-z
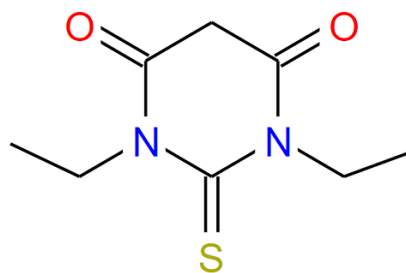
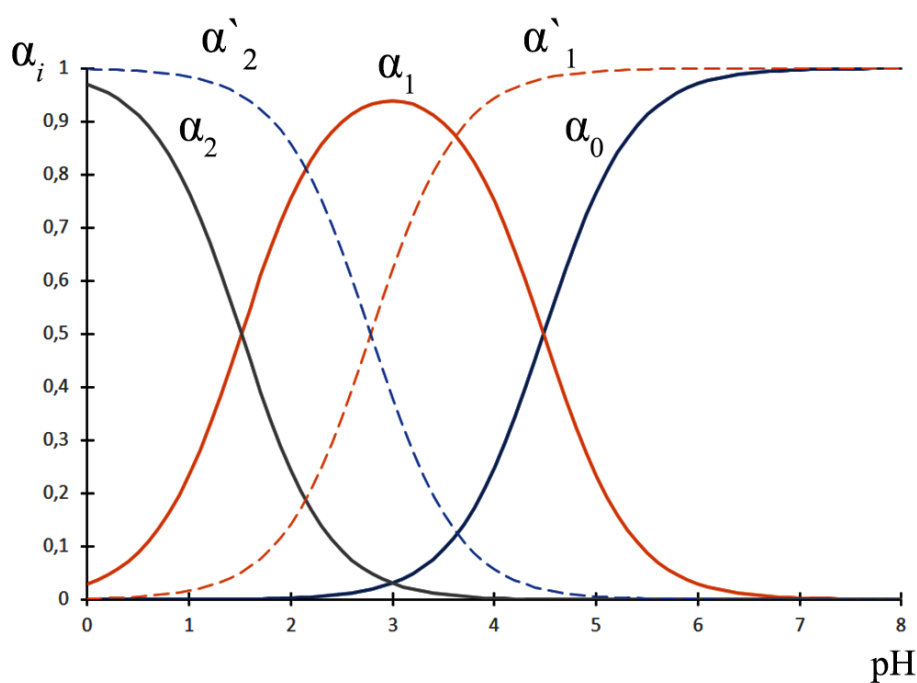**Fig. 1.** Graphical formulas of 1,3-Diethyl-2-thiobarbituric acid (HDetba)

Fig. 2. HDetba and Bipy distribution diagram of species: α_0 – Bipy, α_1 – BipyH$^+$, α_2 – BipyH$_2^{2+}$; $\alpha`_2$ – HDetba, $\alpha`_1$ – Detba$^-$. Here αi is the molar fraction of the i-th species.
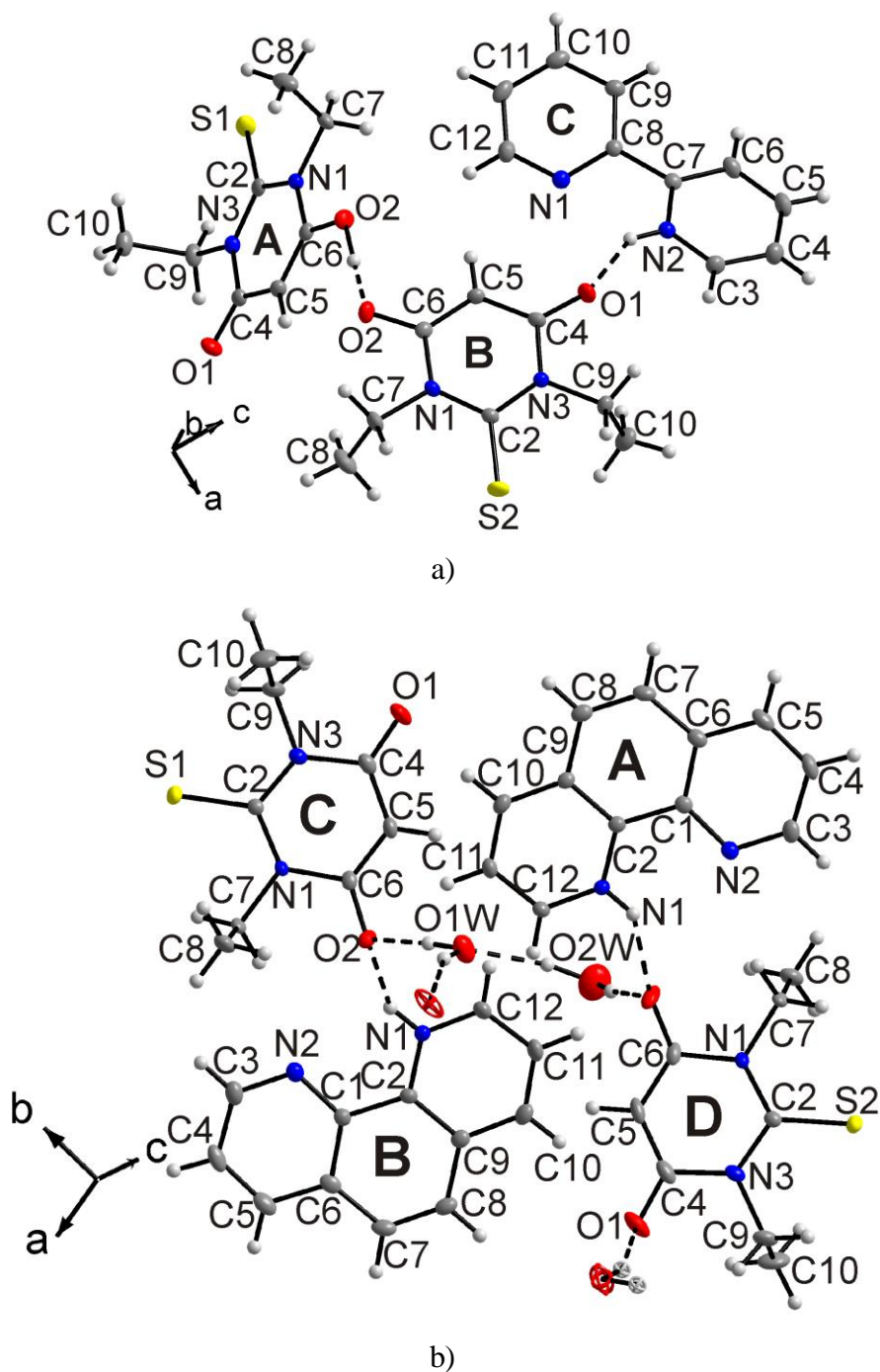
a)

b)

Fig. 3. The asymmetric unit of the (**1**) (a), (**2**) (b) unit cell. Symmetry independent, different molecules are marked by A, B, C, D labels. All atoms in the asymmetric unit are labeled. The neighboring symmetry-generated atoms are represented by principal ellipses with an individual color. The intermolecular hydrogen bonds are represented by dashed lines. The ellipsoids are drawn at the 50% probability level, except for the hydrogen atoms represented by spheres.
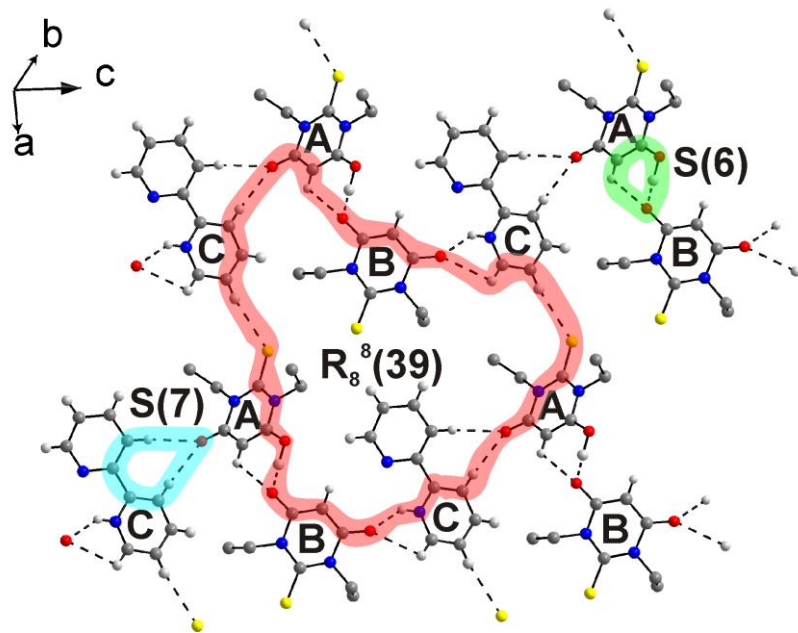
a)
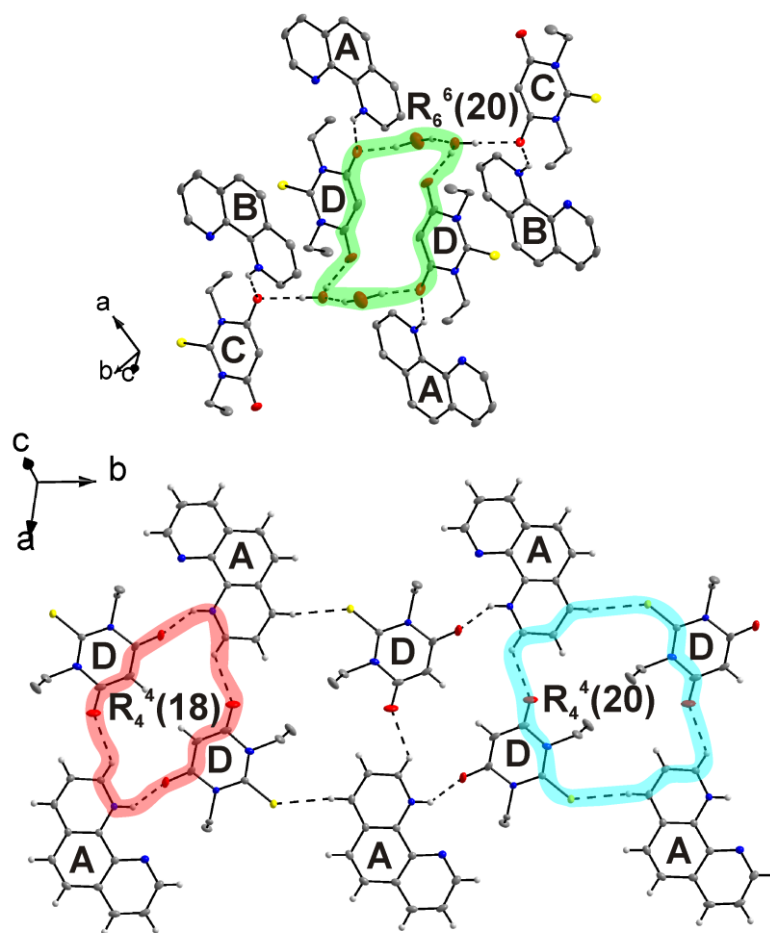
b)

Fig. 4. Hydrogen bonding in (**1**) (a) and (**2**) (b). The H-bonds are marked by dashed lines, the H-bond motifs are marked by circles. Different ions/molecules are marked by A, B, C, D labels. Some H atoms were deleted to simplify the figure.

Supported Information

Table 1S. Main parameters of processing and refinement of the (**1**) and (**2**) samples

Compound	BipyH(Detba)(HDetba) (**1**)
Sp.Gr.	*P*-1
a, Å	10.381 (2)
b, Å	11.070 (2)
c, Å	13.581 (3)
α, °	69.175 (6)
β, °	87.72 (1)
γ, °	72.358 (9)
V, Å^3	1386.1 (4)
2θ-interval, °	5-85
R_{wp}, %	6.84
R_p, %	5.25
R_{exp}, %	4.49
χ^2	1.53

Table 2S. Main geometric parameters (Å, º) of (**1**) and (**2**)

BipyH(Detba)(HDetba) (**1**)		PhenH(Detba)·H$_2$O (**2**)	
S1—C2A	1.6801 (11)	S1—C2C	1.6882 (16)
S2—C2B	1.6769 (11)	S2—C2D	1.6841 (17)
O1A—C4A	1.2390 (15)	O1C—C4C	1.234 (2)
O1B—C4B	1.2439 (17)	O1D—C4D	1.249 (2)
O2A—C6A	1.3040 (13)	O2C—C6C	1.271 (2)
O2B—C6B	1.2841 (13)	O2D—C6D	1.257 (2)
N1A—C2A	1.3765 (13)	N1C—C2C	1.372 (2)
N1B—C2B	1.3731 (13)	N1D—C2D	1.368 (2)
N1A—C6A	1.3932 (14)	N1C—C6C	1.421 (2)
N1B—C6B	1.4021 (13)	N1D—C6D	1.416 (2)
N1A—C7A	1.4793 (15)	N1C—C7C	1.478 (2)
N1B—C7B	1.4823 (18)	N1D—C7D	1.476 (2)
N3A—C2A	1.3686 (14)	N3C—C2C	1.363 (2)
N3B—C2B	1.3710 (16)	N3D—C2D	1.366 (2)
N3A—C4A	1.4226 (14)	N3C—C4C	1.436 (2)
N3B—C4B	1.4170 (14)	N3D—C4D	1.424 (2)
N3A—C9A	1.4766 (14)	N3C—C9C	1.475 (2)
N3B—C9B	1.4750 (14)	N3D—C9D	1.476 (2)
C4A—C5A	1.4094 (14)	C4C—C5C	1.403 (2)
C4B—C5B	1.4014 (14)	C4D—C5D	1.388 (3)
C5A—C6A	1.3666 (17)	C5C—C6C	1.374 (2)
C5B—C6B	1.3770 (18)	C5D—C6D	1.391 (3)
C7A—C8A	1.517 (2)	C7C—C8C	1.511 (2)
C7B—C8B	1.517 (2)	C7D—C8D	1.516 (2)
C9A—C10A	1.521 (2)	C9C—C10C	1.521 (3)
C9B—C10B	1.520 (2)	C9D—C10D	1.514 (3)
C2A—N1A—C6A	121.9 (1)	C2C—N1C—C6C	123.0 (1)
C2B—N1B—C6B	122.7 (1)	C2D—N1D—C6D	123.0 (1)

N1A—C2A—N3A	116.90 (9)	N1C—C2C—N3C	117.0 (1)
N1B—C2B—N3B	116.56 (9)	N1D—C2D—N3D	117.4 (1)
N3A—C2A—S1	121.95 (9)	N3C—C2C—S1	121.9 (1)
N3B—C2B—S2	121.83 (9)	N3D—C2D—S2	121.4 (1)
C2A—N3A—C4A	124.3 (1)	C2C—N3C—C4C	124.1 (1)
C2B—N3B—C4B	124.0 (1)	C2D—N3D—C4D	123.7 (1)
N1A—C2A—S1	121.16 (9)	N1C—C2C—S1	121.1 (1)
N1B—C2B—S2	121.61 (9)	N1D—C2D—S2	121.2 (1)
C4A—C5A—C6A	121.1 (1)	C4C—C5C—C6C	122.60 (15)
C4B—C5B—C6B	121.2 (1)	C4D—C5D—C6D	122.76 (15)

Table 3S. Parameters of the π–π interaction in (**1**) and (**2**)

Cg_i–Cg_j	d(Cg–Cg), Å	α, deg	β, deg	γ, deg	Cg_i_p, Å	Shift, Å
			BipyH(Detba)(HDetba) (**1**)			
$Cg_1 - Cg'_1$	3.7393 (7)	0.02 (5)	25.6	25.6	3.3726 (4)	1.615
$Cg_3 - Cg'_3$	3.5819 (7)	0.00 (6)	22.4	22.4	3.3125 (5)	1.363
$Cg_2 - Cg''_3$	3.4250 (7)	2.62 (6)	14.9	15.7	3.2980 (4)	0.924
			PhenH(Detba)·H_2O (**2**)			
$Cg_1 - Cg'_5$	3.7941 (9)	4.24 (7)	25.3	28.3	3.3409 (6)	1.798
$Cg_2 - Cg'_4$	3.7930 (9)	5.36 (7)	29.5	24.9	3.4393 (6)	1.599
$Cg_2 - Cg'_6$	3.6049 (9)	1.70 (7)	21.4	20.0	3.3883 (6)	1.231
$Cg_3 - Cg'_5$	3.5991 (9)	1.02 (7)	20.0	21.0	3.3611 (6)	1.287
$Cg_3 - Cg'_6$	3.5769 (9)	0.68 (7)	20.6	20.7	3.3452 (6)	1.266
$Cg_3 - Cg'_8$	3.5307 (9)	10.80 (7)	26.1	15.3	3.4059 (6)	0.930
$Cg_5 - Cg'_7$	3.9723 (9)	12.43 (7)	33.4	25.6	3.5838 (6)	1.713
$Cg_6 - Cg'_7$	3.5732 (9)	13.42 (7)	22.5	14.8	3.4550 (6)	0.911

(**1**): Cg_1 is the center of the rings in H_2detba, Cg_2 is the center of the ring in Hdetba⁻. Cg_3 is the center of the ring BipyrH⁺. Cg'_1 was obtained from Cg_1 by the transform (1-x,1-y,-z), Cg'_2 was obtained from Cg_2 by the transform (1-x,1-y,-z), Cg'_3 was obtained from Cg_3 by the transform (2-x,1-y,-z). Cg_i_p is the distance between the center of the ring Cg_i in the π-π interaction.

(**2**): Cg_1, Cg_2, Cg_3 and Cg_4, Cg_5, Cg_6 are the centers of the rings in PhenH⁺, Cg_7 and Cg_8 are the centers of the rings Hdetba⁻. Cg'_4, Cg'_5, Cg'_6 were obtained from Cg_4, Cg_5, Cg_6 by the transform (-1+x,y,z), Cg'_7 was obtained from Cg_7 by the transform (2-x,2-y,2-z), Cg'_8 was obtained from Cg_8 by the transform (-x,1-y,1-z).
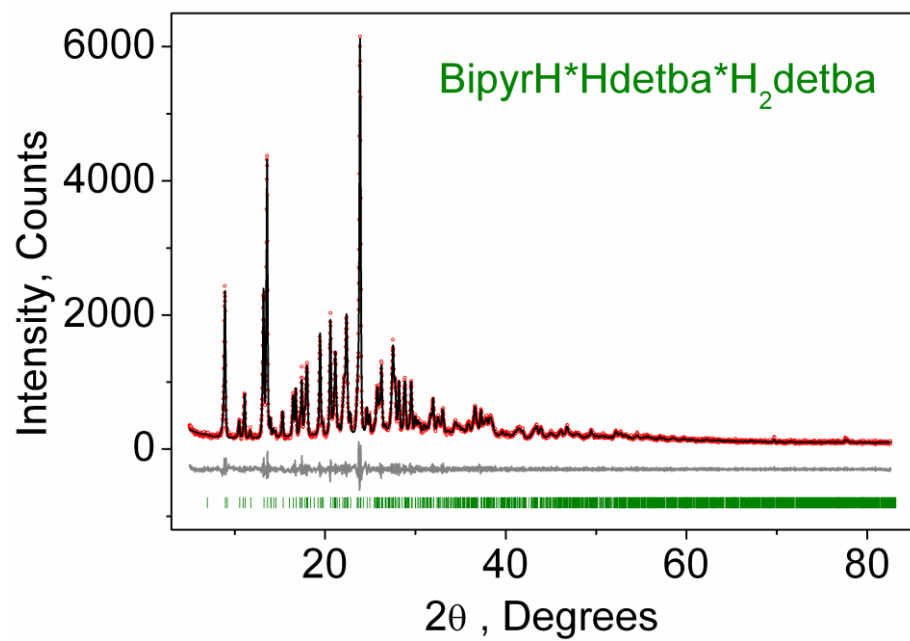
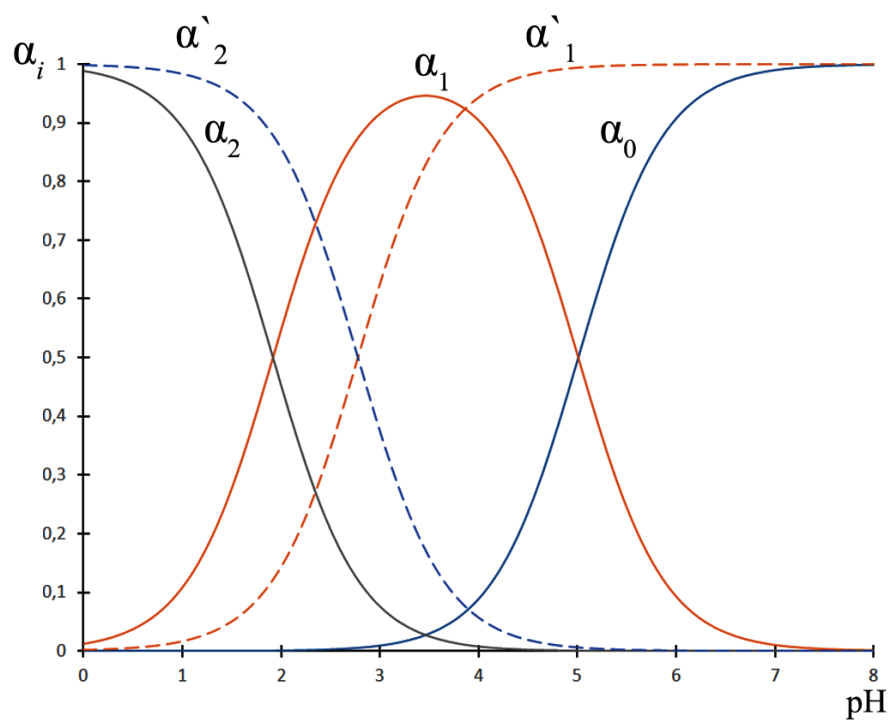**Fig. 1S** Difference X-ray powder patterns of BipyH(Detba)(HDetba) (**1**)

Figure 2S. Phen and HDetba distribution diagram of species molar part (α_i): α_0 − Phen, α_1 − PhenH$^+$, α_2 − PhenH$_2^{2+}$; $\alpha`_2$ −HDetba, $\alpha`_1$ − Detba$^-$
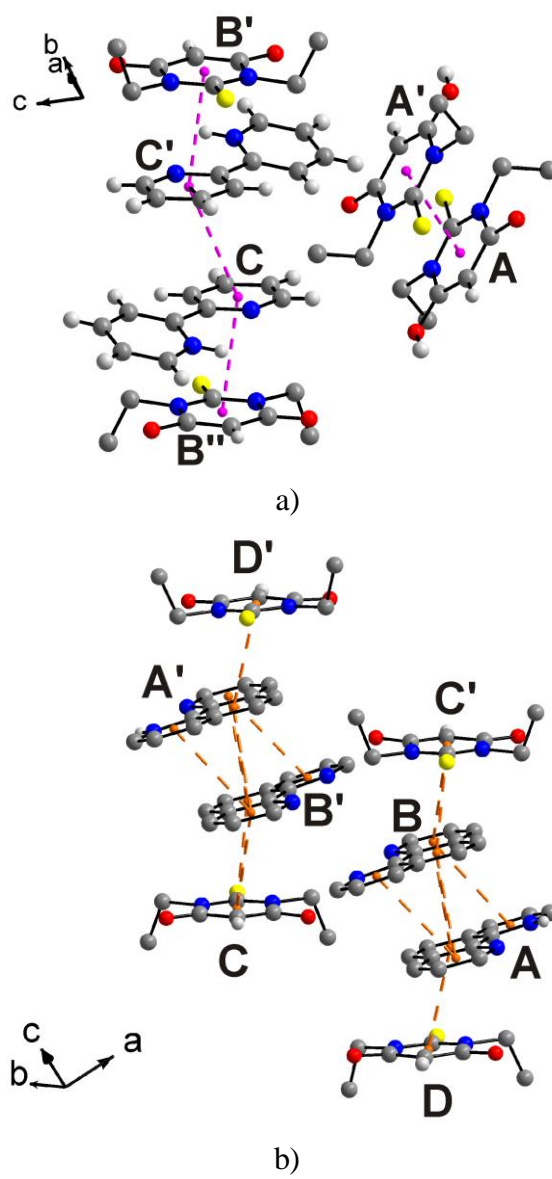
Fig. 3S π-π interactions between ring of the HDetba, Detba⁻, BipyH⁺ ions/molecules in (**1**) (a), between the ring of the Detba⁻ and PhenH⁺ ions in (**2**) (b).

Sample: 01177_NN50_Golovnev
Size: 4.5160 mg
Method: Ramp

DSC-TGA

File: C:\TA\Data\SDT\01177_NN50_Golovnev.001
Operator: Самойло А.С.
Run Date: 31-Jan-2018 12:57
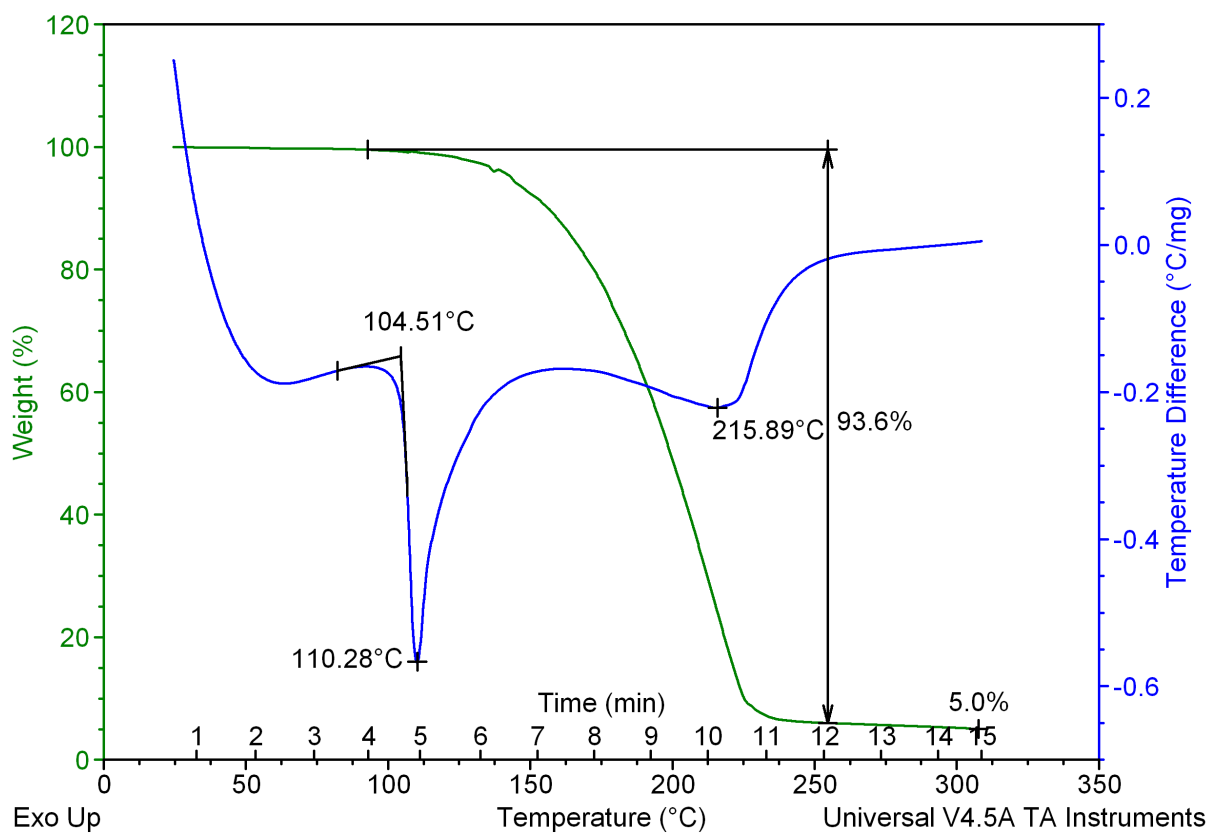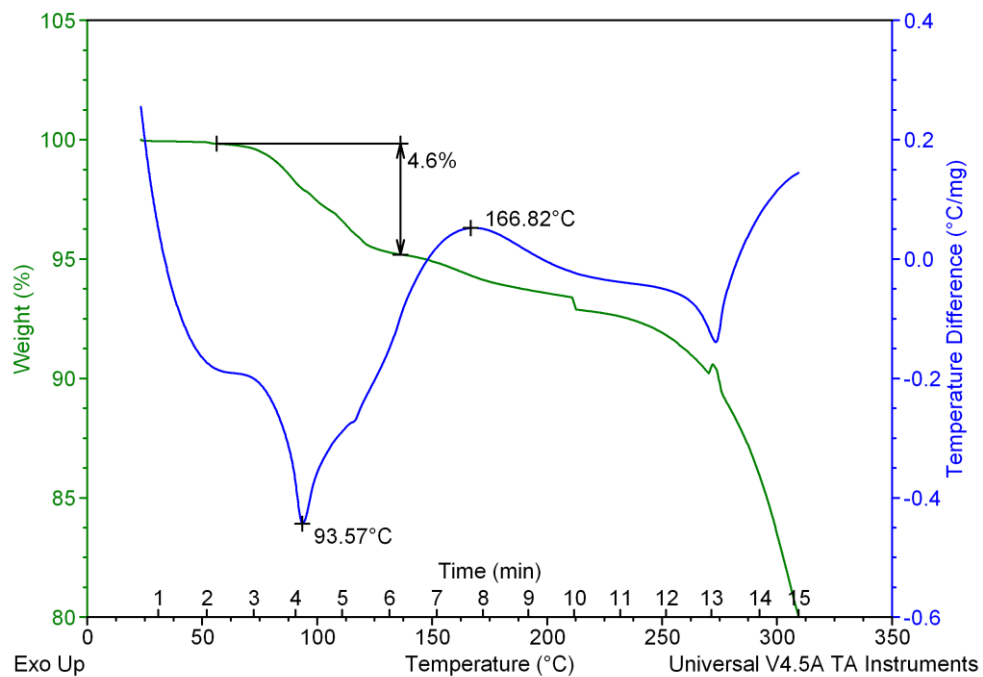Instrument: SDT Q600 V20.5 Build 15

Fig. 4S. TG and DSC curves of (**1**) in air

Fig. 5S. TG and DSC curves of (**2**) in air