Journal of Molecular Structure 1105 (2016) 434–443

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Structural and spectroscopic characterization of 1-(diaminomethylene) thiouron-1-ium benzoate and bis(1-(diaminomethylene)thiouron-1-ium) phthalate trihydrate

Genivaldo Julio Perpétuo [a], Jan Janczak [b, *]

[a] Departamento de Física, Instituto de Ciências Exatas e Biológicas, Universidade Federal de Ouro Preto, 35400-000, Ouro Preto, MG, Brazil
[b] Institute of Low Temperature and Structure Research, Polish Academy of Sciences, PO Box 1410, 50950, Wrocław, Poland

ARTICLE INFO

Article history:
Received 9 July 2015
Received in revised form
21 October 2015
Accepted 26 October 2015
Available online 30 October 2015

Keywords:
1-(diaminomethylene)thiouron-1-ium benzoate
Bis(1-(diaminomethylene)-thiouron-1-ium) phthalate trihydrate
Crystal structure
Hydrogen bonds
Vibrational spectroscopy

ABSTRACT

Two single crystals of 1-(diaminomethylene) thiouron-1-ium benzoate (**1**) and bis(1-(diaminomethylene)thiouron-1-ium) phthalate trihydrate (**2**) were grown using a solution growth technique. The compound **1** crystallises in the centrosymmetric $P2_1/c$ space group of the monoclinic system, whereas the compound **2** in the centrosymmetric *Pbcn* space group of orthorhombic system. The solid-state organisation of **1** and **2** has been analysed with respect to cation-anion and hydrogen bonding interactions. The oppositely charged units interact via almost linear hydrogen bonds with the graphs of $R_2^2(8)$ and $R_2^1(6)$ forming molecular complexes. In the crystal **1** the $R_2^2(8)$ motif is formed by donation to the carboxylate group from amine group joined to C1 and from imine group and $R_2^1(6)$ motif is formed by donation to the O2 from amine group joined to C2 and from imine group, whereas in crystal **2** the graphs are formed oppositely. Interactions between the hydrogen-bonded molecular complexes in **1** lead to formation of layered 2D structure, whereas in **2**, due to presence of hydrated water molecules lead to formation of 3D hydrogen-bonded supramolecular network. The obtained deuterated analogues of **1** and **2** crystallise similar as H-compound in the monoclinic and orthorhombic system with quite similar lattice parameters. The compounds were also characterised by the FT-IR and Raman spectroscopies. The characteristic bands of the functional and skeletal groups are discussed.

1. Introduction

Crystal engineering involving a combination of synthesis and structural chemistry is a branch of material science that rapidly expanding over the past two decades [1,2]. The accurate prediction of a structure and the properties of a product from the structures of basic substrates, which can be considered a designing process, remains the ultimate goal [3]. The exploration of new supramolecular structures and interactions responsible for such an arrangement brings much useful information concerning factors important in structure formation that are helpful in the design process [4]. The hydrogen bonds and other non-covalent intermolecular interactions are of fundamental key for molecular recognition in supramolecular synthesis of new solids [5].

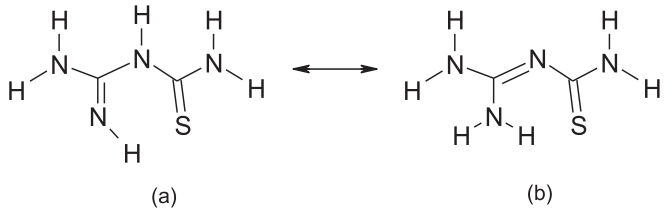
A productive strategy in crystal engineering and control of crystal architecture is to build supramolecular structures from molecules containing complementary arrays of hydrogen bonding sites [6]. The supramolecular synthon of hydrogen-bonding pattern is an effective approach for structural design of solids [7]. Commercially available 2-imino-4-thiobiuret (Aldrich, CAS No. 2114-20-05) is, as has been shown by the X-ray analysis, it tautomeric form of 1-(diaminomethylene)thiourea (Scheme 1) [8].

Both tautomers are useful in crystal engineering as building blocks, since they contain hydrogen-bonding sites. Additionally, both tautomers can act as *N,N*- or *N,S*-coordinating ligands forming several types of complexes with metal ions [9]. The 1-(diaminomethylene)-thiourea contains the basic N atom, therefore it can forms slats with organic and inorganic acids forming extended hydrogen-bonding networks in solids [10]. The supramolecular aggregation pattern of 1-(diaminomethylene)-thiourea with tartaric acid and its deuterated analogue are examples of supramolecular hydrogen-bonding networks in solids that can be utilised as materials for non-linear optics [11].

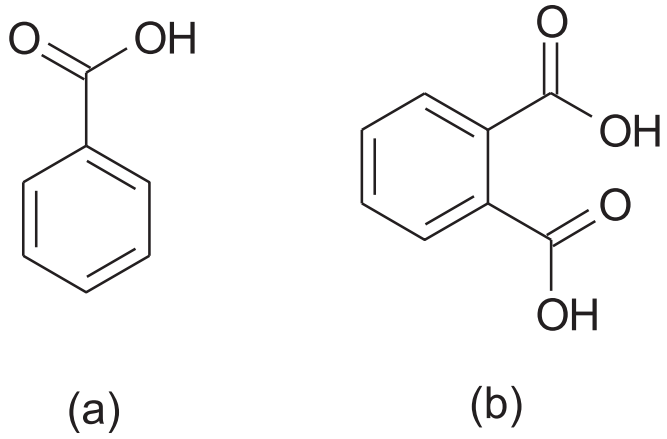
To explore the usefulness of 1-(diaminomethylene)-thiourea as

* Corresponding author.
E-mail address: j.janczak@int.pan.wroc.pl (J. Janczak).

http://dx.doi.org/10.1016/j.molstruc.2015.10.080
0022-2860/



Scheme 1. Tautomeric equilibrium between 2-imino-4-thiobiuret (a) and 1-(diaminomethylene)-thiourea (b).



Scheme 2. Benzoic acid (a) and phthalic acid (b).

a building block in supramolecular synthesis, in the present work we investigate the supramolecular architecture formed by self-assembly of 1-(diaminomethylene)-thiourea with benzoic and phthalic acids (Scheme 2). This study is aimed into the interaction between the building blocks formed the supramolecular architecture in solids. Both compounds were also characterised by vibrational spectroscopy. Assignment of the bands has been supported by the comparison of the IR-spectra of protiated compounds with the IR-spectra of deuterated analogues.

2. Experimental

2-imino-4-thiobiuret, benzoic acid and phthalic acid were commercially available and used as received. Elemental analysis was carried out with a Perkin–Elmer 240 elemental analyser.

2.1. Preparation of 1-(diaminomethylene)thiouron-1-ium benzoate (1) and its deuterated analogue

Commercially available 2-imino-4-thiobiuret (Aldrich, CAS No. 2114-02-05), which is in fact the tautomeric form 1-(diaminomethylene)thiourea (0.118 g) and the benzoic acid (0.122 g) were added to hot water in a molar proportion of 1:1. When the solution became homogeneous it was cooled slowly and kept at room temperature. After several days, transparent colourless crystals of $C_6H_5COO{\cdot}C_2H_7N_4S$ (**1**) were formed. Analysis: calculated for $C_8H_{12}N_4SO_2$: C, 44.98; N, 23.32; O, 13.32; S, 13.34 and H, 5.03%. Found: C,45.11; N, 23.22; O, 13.45; S, 13.22, and H, 5.00%. Deuterated analogue of 1-(diaminomethylene)thiouron-1-ium benzoate was prepared by the usual reaction with heavy water. The crystals of 1-(diaminomethylene)thiouron-1-ium benzoate were dissolved in heavy water, and left in the atmosphere saturated with heavy water for one weak, in order to avoid the contamination of the crystals. Next the procedure was repeated twice.

2.2. Preparation of bis(1-(diaminomethylene)thiouron-1-ium) phthalate trihydrate (2) and its deuterated analogue

2-imino-4-thiobiuret (0.118 g) and phthalic acid (0.166 g) were dissolved in hot water in a molar proportion of 1:1. The solution was cooled and kept at the room temperature. After several days, colourless single crystals of bis(1-(diaminomethylene)thiouron-1-ium) phthalate trihydrate (**2**) were obtained. Analysis: calculated

Table 1
Crystallographic data for 1-(diaminomethylene)thiouron-1-ium benzoate (**1**) and bis(1-(diaminomethylene)thiouron-1-ium) phthalate trihydrate (**2**).

	1	**2**
Empirical formula	$C_9H_{12}N_4O_2S$	$C_{12}H_{24}N_8O_7S_2$
Formula weight (g mol^{-1})	240.29	456.51
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$ (No. 14)	$P\,b\,c\,n$ (No. 60)
a (Å)	17.400 (4)	7.9170 (16)
b (Å)	4.9390 (10)	14.130 (3)
c (Å)	13.424 (3)	18.293 (4)
β (°)	99.13 (3)	
V (Å^3)	1139.0 (4)	2046.4 (7)
Z	4	4
D_{calc}/D_{obs} (g cm^{-3})	1.401/1.40	1.482/1.48
μ (mm^{-1})	0.276	0.313
Crystal size (mm)	0.28 × 0.14 × 0.12	0.32 × 0.24 × 0.10
Radiation type, wavelength, λ (Å)	Mo $K\alpha$, 0.71073	Mo $K\alpha$, 0.71073
Temperature (K)	295 (2)	295 (2)
θ range(°)	3.07 ÷ 29.54	3.09 ÷ 29.59
Absorption correction	Numerical, CrysAlis Red	Numerical, CrysAlis Red
T_{min}/T_{max}	0.9292/0.9651	0.9112/0.9708
Refls collected/unique/observed	12998/2958/1546	21484/2711/1685
R_{int}	0.0572	0.0534
Refinement on	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0437	0.0374
$wR(F^2$ all reflections)	0.0627	0.0677
Goodness-of-fit, S	0.989	1.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	+0.162, −0.201	+0.218, −0.189

$wR = \{\Sigma\,[w(F_o^2 - F_c^2)^2]/\Sigma wF_o^4\}^{½}$; $w^{-1} = 1/[\sigma^2(F_o^2) + (aP)^2]$ where $a = 0.01$ and $a = 0.024$ for 1 and 2, respectively, and $P = (F_o^2 + 2F_c^2)/3$.

for $C_{12}H_{24}N_8O_7S_2$: C, 31.57; N, 24.55; O, 24.53; S, 14.05; and H, 5.30%. Found: C, 31.48; N, 24.60; O, 24.65; S 14.00, and H, 5.27%. Deuterated analogue of bis(1-(diaminomethylene)thiouron-1-ium) phthalate trihydrate was prepared by the usual reaction with heavy water, and left in the atmosphere saturated with heavy water for one weak, in order to avoid the contamination of the crystals. Next the procedure was repeated twice.

2.2.1. X-ray data collection

X-ray intensity data for the **1** and **2** single crystals were collected using graphite monochromatic Mo Kα radiation on a four-circle κ geometry KUMA KM-4 diffractometer with a two-dimensional area CCD detector. The ω-scan technique with $\Delta\omega = 1.0^\circ$ for each image was used for data collection. The 900 images for six different runs covering over 99% of the Ewald sphere were performed. One image was used as a standard after every 50 images for monitoring of the crystals stability and the data collection. No correction on the relative intensity variations was necessary. Data collections were made using the CrysAlis CCD program [12]. Integration, scaling of the reflections, correction for Lorentz and polarisation effects and absorption corrections were performed using the CrysAlis Red program [12]. The structures were solved by the direct methods using SHELXS-97 and refined using SHELXL-97 program [13]. The hydrogen atoms involving in the hydrogen bonds were located in difference Fourier maps and were refined. The hydrogen atoms joined to aromatic carbon atoms were introduced in their geometrical positions. The final difference Fourier maps showed no peaks of chemical significance. Details of the data collection parameters, crystallographic data and final agreement parameters are collected in Table 1. Visualisations of the structures were made with the Diamond 3.0 program [14]. Selected geometrical parameters are listed in Table 2 and the geometry of hydrogen bonding interactions is collected in Table 3. The obtained deuterated analogues of **1** and **2** crystallise similar as H-compounds in the same crystal system with quite similar lattice parameters.

Table 2
Selected bond lengths (Å) and angles (°) 1-(diaminomethylene)thiouron-1-ium benzoate (**1**) and bis(1-(diaminomethylene)thiouron-1-ium) phthalate trihydrate (**2**).

	1	**2**
C1–S1	1.679 (2)	1.6640 (15)
C1–N1	1.381 (3)	1.3837 (18)
C1–N2	1.312 (3)	1.3216 (19)
C2–N1	1.366 (3)	1.3609 (18)
C2–N3	1.309 (3)	1.3214 (19)
C2–N4	1.311 (3)	1.3008 (19)
C3–O1	1.267 (2)	1.2706 (16)
C3–O2	1.244 (2)	1.2492 (16)
C3–C4	1.511 (3)	1.5025 (19)
N2–C1–N1	112.7 (2)	112.72 (13)
N2–C1–S1	122.8 (2)	121.42 (12)
N1–C1–S1	124.5 (2)	125.86 (12)
C2–N1–C1	131.4 (2)	130.07 (13)
N3–C2–N4	121.5 (2)	120.43 (15)
N3–C2–N1	115.5 (2)	116.51 (14)
N4–C2–N1	123.1 (2)	123.06 (14)
O2–C3–O1	125.2 (2)	124.25 (14)

Table 3
(a) Hydrogen-bond geometry (Å, °) for 1-(diaminomethylene)thiouron-1-ium benzoate (**1**) and (b) for bis(1-(diaminomethylene)thiouron-1-ium) phthalate trihydrate (**2**).

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
(a) **1**				
N1–H1···O2	0.89 (2)	1.89 (2)	2.769 (2)	165 (2)
N2–H21···O1	0.97 (2)	1.85 (2)	2.806 (2)	169 (2)
N2–H22···S1^{i}	0.88 (2)	2.50 (2)	3.368 (2)	168 (2)
N3–H31···O1^{ii}	0.87 (2)	1.98 (2)	2.776 (3)	152 (2)
N3–H32···O2	0.84 (2)	2.17 (2)	2.896 (3)	145 (2)
N4–H41···O1^{ii}	0.84 (2)	2.16 (2)	2.900 (3)	148 (2)
N4–H42···S1	0.87 (2)	2.32 (2)	3.025 (2)	138 (2)
(b) **2**				
N1–H1···O1	0.83 (2)	1.94 (2)	2.762 (2)	170 (2)
N2–H12···O1	0.86 (2)	2.46 (2)	3.190 (2)	143 (2)
N2–H22···O2^{i}	0.90 (2)	2.09 (2)	2.966 (2)	165 (2)
N3–H13···O2	0.89 (2)	2.06 (2)	2.945 (2)	177 (2)
N3–H23···O3^{ii}	0.85 (2)	2.36 (3)	3.078 (2)	143 (2)
N3–H23···S1^{iii}	0.85 (2)	2.90 (3)	3.443 (2)	124 (2)
N4–H14···O3^{ii}	0.86 (2)	2.06 (2)	2.880 (2)	159 (2)
N4–H24···S1	0.86 (2)	2.29 (2)	3.008 (2)	140 (2)
O3–H2···O4	0.87 (1)	1.94 (1)	2.801 (2)	170 (2)
O3–H3···O2^{iv}	0.86 (1)	2.16 (1)	3.013 (2)	171 (2)
O4–H4···O1	0.87 (1)	1.86 (1)	2.721 (2)	171 (2)

Symmetry codes for crystal **1**: (*i*) $-x+1, -y+2, -z+1$; (*ii*) $x, -y+3/2, z-1/2$. Symmetry codes for crystal **2**: (*i*) $x-1, y, z$; (*ii*) $-x+1/2, -y+1/2, z+1/2$; (*iii*) $x+1, y, z$; (*iv*) $x-1/2, y+1/2, -z+1/2$.

2.2.2. X-ray powder diffraction

The protiated and deuterated samples of **1** and **2** were measured on a PANanalytical X'Pert diffractometer equipped with a Cu-Kα radiation source ($\lambda = 1.54182$ Å) at room temperature.

2.2.3. Vibrational spectra measurements

The vibrational measurements of **1** and **2** and theirs deuterated

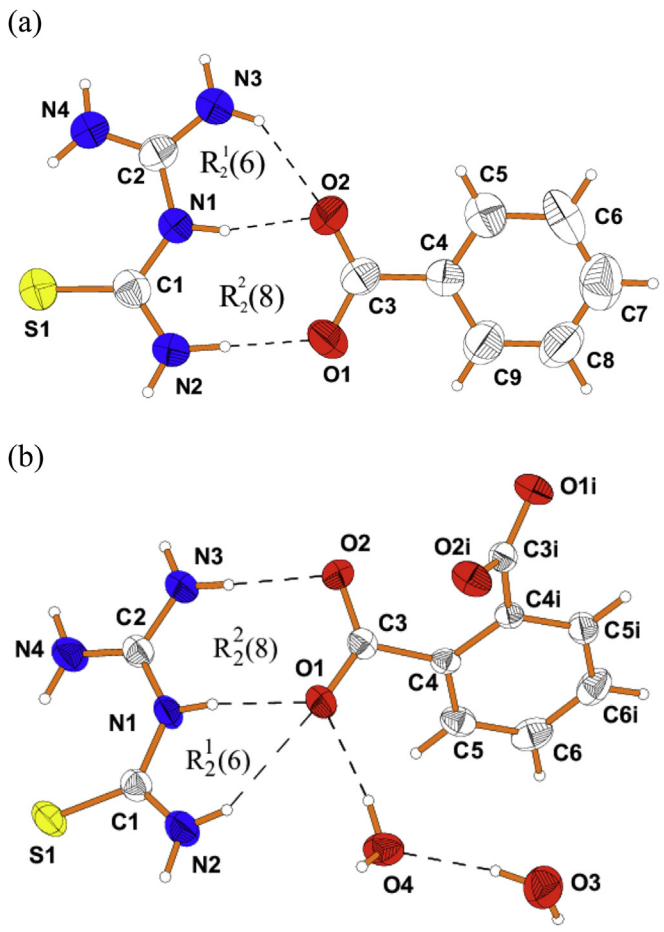


Fig. 1. A view of 1-(diaminomethylene)thiouron-1-ium benzoate (a), bis(1-(diaminomethylene)thiouron-1-ium phthalate trihydrate (b) showing displacement ellipsoids at the 50% probability level and H atoms as a sphere of arbitrary radii. Dashed lines represent the hydrogen bonds. Symmetry code: (*i*) 2−x, y, 1.5−z.

analogues were carried out at room temperature. The Fourier transform infrared spectra were recorded from nujol mulls between 4000 and 400 cm^{-1} on a Bruker IFS 113 V FTIR spectrometer. Resolution was set up to 2 cm^{-1}. The Fourier Transform Raman spectrum was recorded on a FRA-106 attached to the Bruker 113 V FTIR spectrometer equipped with Ge detector cooled to liquid nitrogen temperature. Resolution was set up to 2 cm^{-1}, signal/noise ratio was established by 32 scans. Nd^{3+}-YAG air-cooled diode pumped laser of power ca. 200 mW was used as an exciting source. The incident laser excitation was 1064 nm. The scattered light was collected at the angle of 180° in the region of 3600–80 cm^{-1}, resolution 2 cm^{-1}, 256 scans.

3. Results and discussion

Good quality single crystals of 1-(diaminomethylene) thiouron-1-ium benzoate (**1**) and bis(1-(diaminomethylene)thiouron-1-ium) phthalate trihydrate (**2**) suitable for the X-ray single crystal analysis were obtained from water solutions at ambient temperature. The 1-(diaminomethylene) thiouron-1-ium benzoate crystallises in the centrosymmetric space group $P2_1/c$ of monoclinic system whereas bis(1-(diaminomethylene)thiouron-1-ium) phthalate trihydrate crystallises in the centrosymmetric space group P*bcn* of the orthorhombic system. The deuterated analogues were obtained by usual reaction of protiated crystals with heavy water. The deuterated analogues also crystallise as the protiated compounds in the

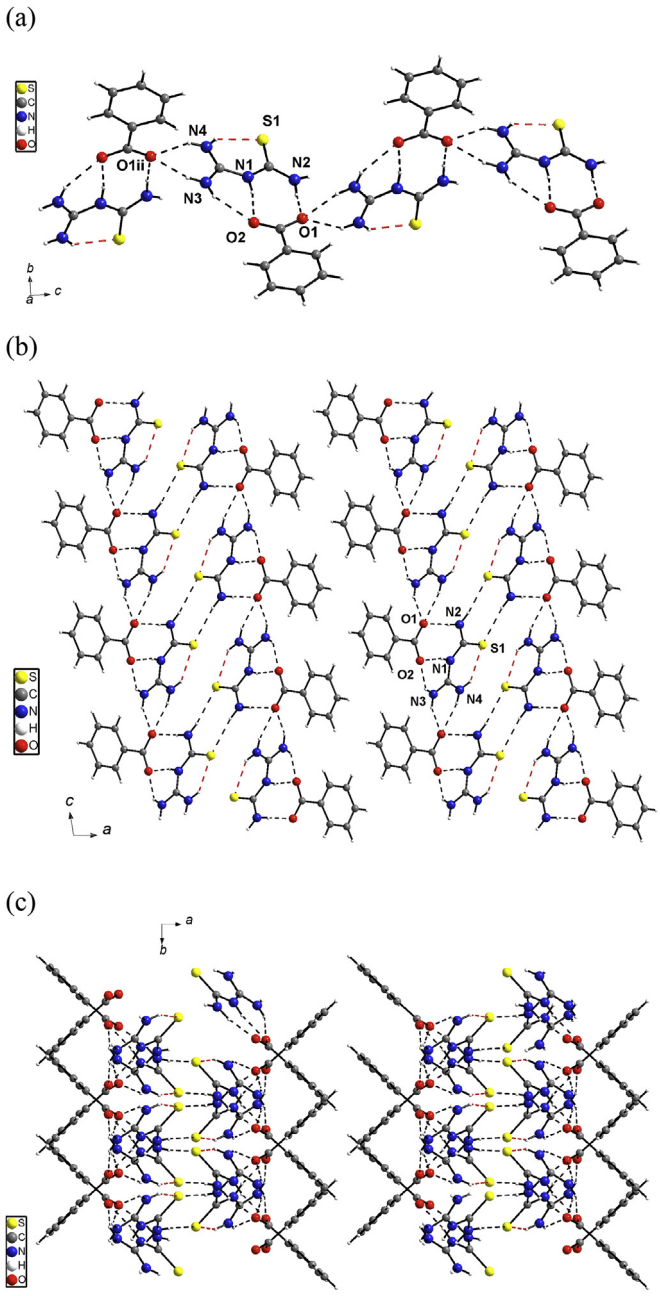


Fig. 2. A view of hydrogen bonded chain of 1-(diaminomethylene)thiouron-1-ium benzoate (a) and the two dimensional hydrogen-bonding layers of 1-(diaminoethylene)hiouron-1-ium benzoate viewed along *b*-axis (b) and *c*-axis (c).

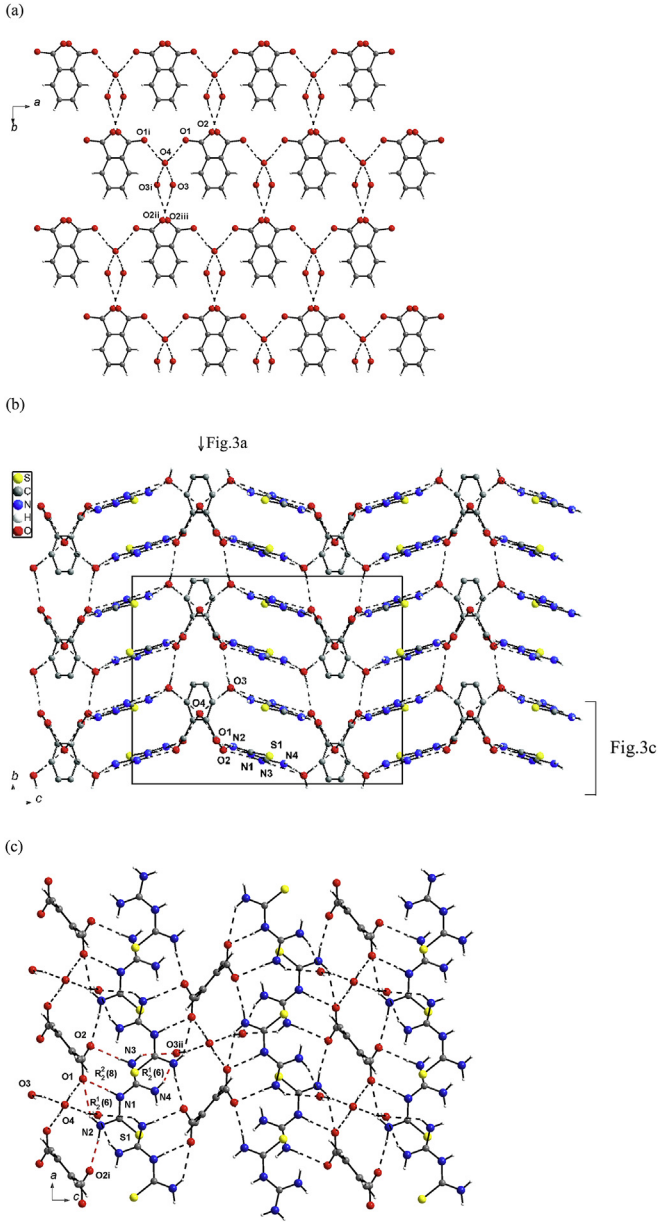


Fig. 3. The anionic 2D-layer of hydrogen bonded by water molecules of phthalate(2-) anions viewed along *c*-axis, symmetry codes (*i*) −x, y, 0.5-z; (*ii*) −0.5 + x, 0.5 + y, 0.5 + z; (*iii*) 0.5−x, 0.5 + y, z (a), 3D hydrogen bonded supramolecular network of bis(1-(diaminomethylene)thiouron-1-ium phthalate trihydrate viewed along *a*-axis (b) and the undulating layer viewed along *b*-axis, symmetry codes: (*i*) *x*−1, *y*, *z*; (*ii*) −*x*+0.5, −*y*+0.5, *z*+0.5 (c).

same space groups with quite similar lattice parameters, so the protiated and deuterated crystals of **1** and **2** are isostructural and was confirmed by the powder X-ray diffraction experiments (Figs. S1 and S2 in supplementary material). The microscopic images of **1** and **2** crystals are shown in Figs. S3 and S4 in supplementary material.

The X-ray single crystal analysis of **1** and **2** shows that the carboxylate groups are deprotonated, and the proton is transferred to the central N1 atom of 1-(diaminomethylene) thiourea molecule forming 1-(diaminomethylene) thiouron-1-ium cation. The oppositely charged units interact via almost linear hydrogen bonds with the graphs of $R_2^2(8)$ and $R_2^1(6)$ forming molecular complexes as illustrate in Fig. 1. In the crystal **1** the $R_2^2(8)$ motif is formed by donation to the carboxylate group from amine group joined to C1 and from imine group and $R_2^1(6)$ motif is formed by donation to the O2 from amine group joined to C2 and from imine group (Fig. 1a), whereas in crystal **2** the graphs are formed oppositely. In addition, in the hydrated crystals **2**, hydrogen bonded water dimer interacts with O1 atom of COO^- group via O–H···O hydrogen bond (Fig. 1b).

The conformation of the 1-(diaminomethylene)thiouron-1-ium cation in the crystals **1** and **2** is not strictly, but twisted. Both arms of the cation are oppositely rotated around the C–N bonds involving the central N1 atom. The dihedral angle between the N1/C1/S1/N2 and N1/C2/N3/N4 planes is equal to 3.1 (1)° in crystal **1** and 1.8 (1) in crystal **2**. The dihedral angle in the present structures is significantly smaller than that in the crystal of neutral 1-(diaminomethylene)thiourea (22.2(1)°) [8]. The currently available data on 1-(diaminomethylene)thiouron-1-ium salts [15] show that the cation twisting may differ when different anions are used (1.4 (1)° for 1-(diaminomethylene)thiouron-1-ium perchlorate [10b] to 22.9 (1)° for 1-(diaminomethylene)thiouron-1-ium chloride [10a]) and is undoubtedly dependent on the hydrogen bonding system formed by the oppositely charged units. The gas-phase conformation of the 1-(diaminomethylene)thiouron-1-ium cation as show the *ab-initio* MO calculations is also twisted with similar dihedral angle of 6.2° [10a]. The C1–S1 bond (Table 2) is slightly longer than the typical C=S double bond as observed in the thioformaldehyde $CH_2C{=}S$ (1.6019 (8) Å) [16], which represents 100% double-bond character. The three C–N bonds linking the amine groups of the 1-(diaminomethylene)thiouron-1-ium cation in both crystals (**1** and **2**) are shorter than the C–N bonds involving the central N1 atom (Table 2). The planarity of the amine groups points to the sp^2

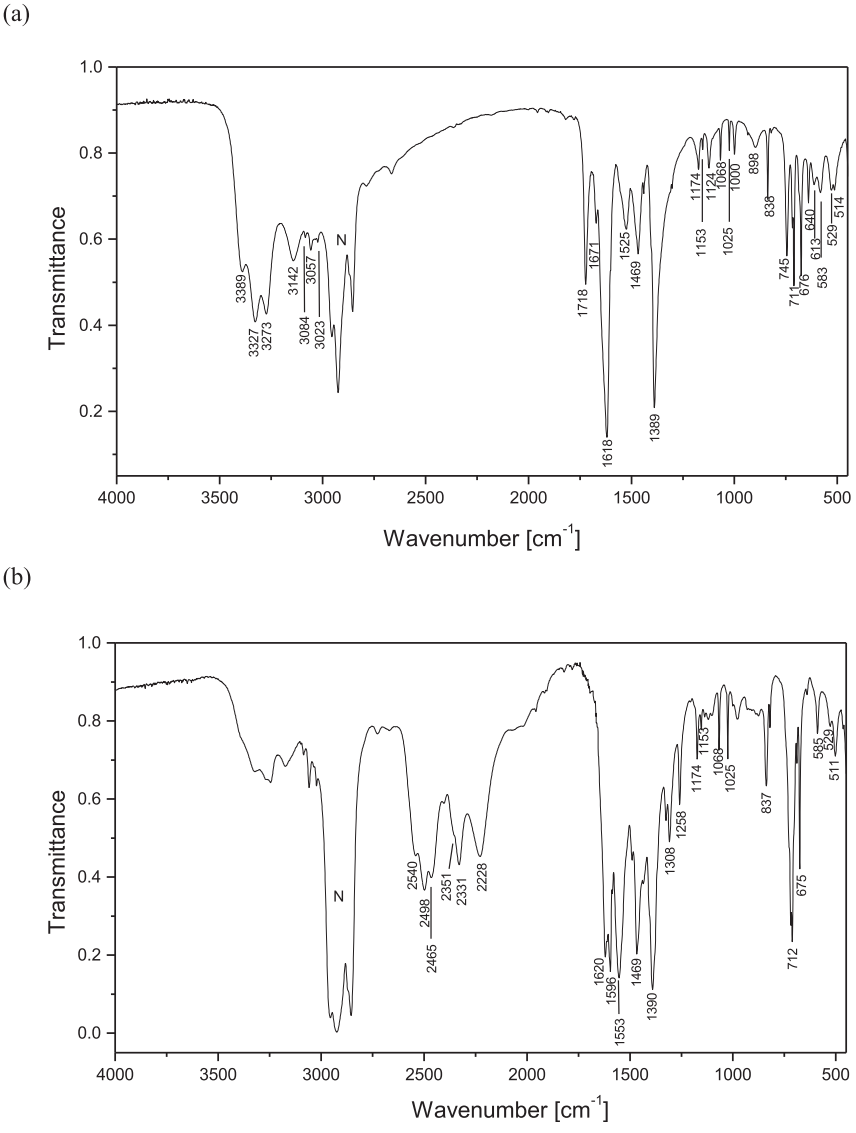


Fig. 4. IR-spectrum of protiated (a) and deuterated analogue (b) of 1-(diaminomethylene)thiouron-1-ium benzoate.

hybridisation of the orbitals on the amine nitrogen atoms and the lone pair of electron localised on the *p* orbital. Therefore the partial delocalisation of the lone pair on *p* orbital of the amine groups and of the π bond of the double C1=S1 and C2=N1 bonds is possible and leads to shortening of other C–N bonds linking the amine groups and to the elongation of the C1=S1 and C2=N1 bonds (Table 2).

The geometrical parameters of the anionic parts of the crystals, i.e. benzoate(−) and phthalate (2-), do not deviate significantly from the reported values in the other structures containing these anions [15]. The C–O bond lengths of the COO^- groups (Table 2) point on delocalisation of the π-bond and the charge over both C–O bonds. The COO^- group of benzoate(−) anion is not coplanar with the benzene ring. It is slightly rotated around the C3–C4 bond. The dihedral angle between the planes of COO^- and benzene ring is equal to 10.2 (1)°. This is in contrast to the planar conformation of benzoic acid in crystal due to formation of the hydrogen-bonded dimer [17]. The non-planar phthalate (2-) anion has twofold symmetry axis running in the centre of the C4–$C4^i$ and C6–$C6^i$ bonds (symmetry code as in Fig. 1) with the COO^- groups oppositely rotated around the C3–C4 or $C3^i$–$C4^i$ by ± 48.8 (1)°. The rotation angles are greater than that observed in the crystal of pure phthalic acid ~30.5° [18] due to the repulsive forces between deportonated COO^- groups.

In the crystal **1**, the hydrogen bonding interactions (Table 3a) between the *c*-glide plane related cation-anion molecular complexes lead to formation of chains along the *c*-axis (Fig. 2a). Inversion related chains are arranged parallel to (100) plane forming two dimensional supramolecular layers (Fig. 2b and c). Within the layers the inversion-related chains interact each other via N–H···S hydrogen bonds with a graph of $R_2^2(8)$. The importance of such interactions has been questioned [19]. However, the D–H···S interactions (D = donor) are important in the biological systems due to presence of high content of S atom in biological molecules. In addition, the N–H···S interactions have been utilised for design supramolecular arrangement of thiourea derivatives [20]. Therefore, such N–H···S interactions seem to be important in the present structure (Table 3), where the formation of the intramolecular N–H···S interactions is favoured by the six-membered hydrogen-bonded ring with a graph of S(6) and the intermolecular eight-membered hydrogen-bonded ring with a graph of $R_2^2(8)$; the presence of C=S bonds makes it some resonance-assisted

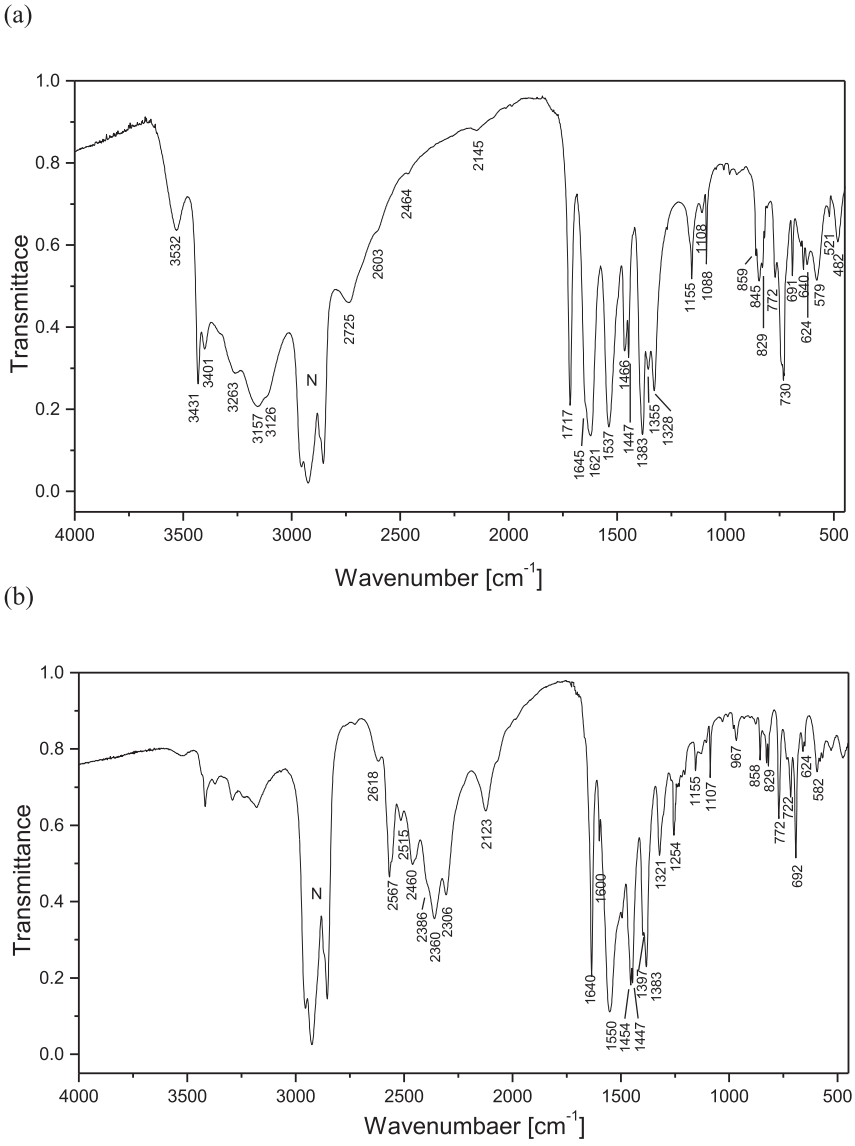


Fig. 5. IR-spectrum of protiated (a) and deuterated analogue (b) of bis(1-(diaminomethylene)thiouron-1-ium phthalate trihydrate.

stabilisation. The possibility of resonance-induced hydrogen bond ring formation with the S atom of a C=S group with N substituents has been mentioned by Allen et al. [21]. However, in this structure the hydrogen bonds involving the S atom seem to be driven by the stronger N–H···O and O–H···O hydrogen bonds (Table 3). Neighbouring, N–H···S hydrogen bonded two-dimensional tapes related via translation along the *a*-axis interact mainly via van der Waals forces, since there are no directional interactions between the successive layers (Fig. 2c). There are no π–π interactions between the aromatic rings of the benzoate anions, since the centre gravity of the rings are separated by 4.939 (4) Å.

In the crystal **2**, due to presence of the water molecules, the phthalate(2-) anions are interconnected by water molecules via O–H···O into 2D-layers. Transitionally related along *a*-axis phthalate(2-) anions interact as acceptors with water molecules (O4) forming hydrogen bonded chains aligned along the [100] direction (O1···H–O4–H···O1^{i}, see Fig. 3a). Neighbouring chains related by *n*-glide plane are combined together by the water molecules (O3). The water molecules O3 are donors in the O–H···O hydrogen bonds, whereas as acceptors play the oxygen atoms (O1) of carboxylate groups of one chain and the water molecules (O4) of the other chain. The interconnected chains in such manner form anionic O–H···O hydrogen bonding layers parallel to (001) plane (Fig. 3a). Neighbouring, inversion related water-phthalate(2-) anionic layers are located parallel to (001) plane at z = ¼ and ¾ (Fig. 3b). The successive O–H···O hydrogen bonding anionic layers are interconnected by 1-(diaminomethylene)thiouron-1-ium cations *via* N–H···O hydrogen bonds (Table 3b) into three-dimensional supramolecular network (Fig. 3b). The 1-(diaminomethylene)thiouron-1-ium cations are alternatively linked *via* N–H···O hydrogen bonds with $R_2^2(8)$ and $R_2^1(6)$ graphs to the one anionic layer and with $R_2^1(6)$ graph to the other anionic layer as illustrated in Fig. 3c forming undulating layer. Repetitive occurrence of O3–H3···O2^{iv} hydrogen bonds link the undulating layers forming three-dimensional supramolecular network (Fig. 3b). Between the aromatic rings of phthalate anions there are no π–π interactions, since the center gravity of the rings are separated by 7.917 (3) Å.

The FT-IR spectra of protiated and deuterated analogue of 1-(diaminomethylene)thiouron-1-ium benzoate and bis(1-(diaminomethylene)thiouron-1-ium) phthalate trihydrate are shown in Figs. 4 and 5, respectively, whereas the Raman spectra of the

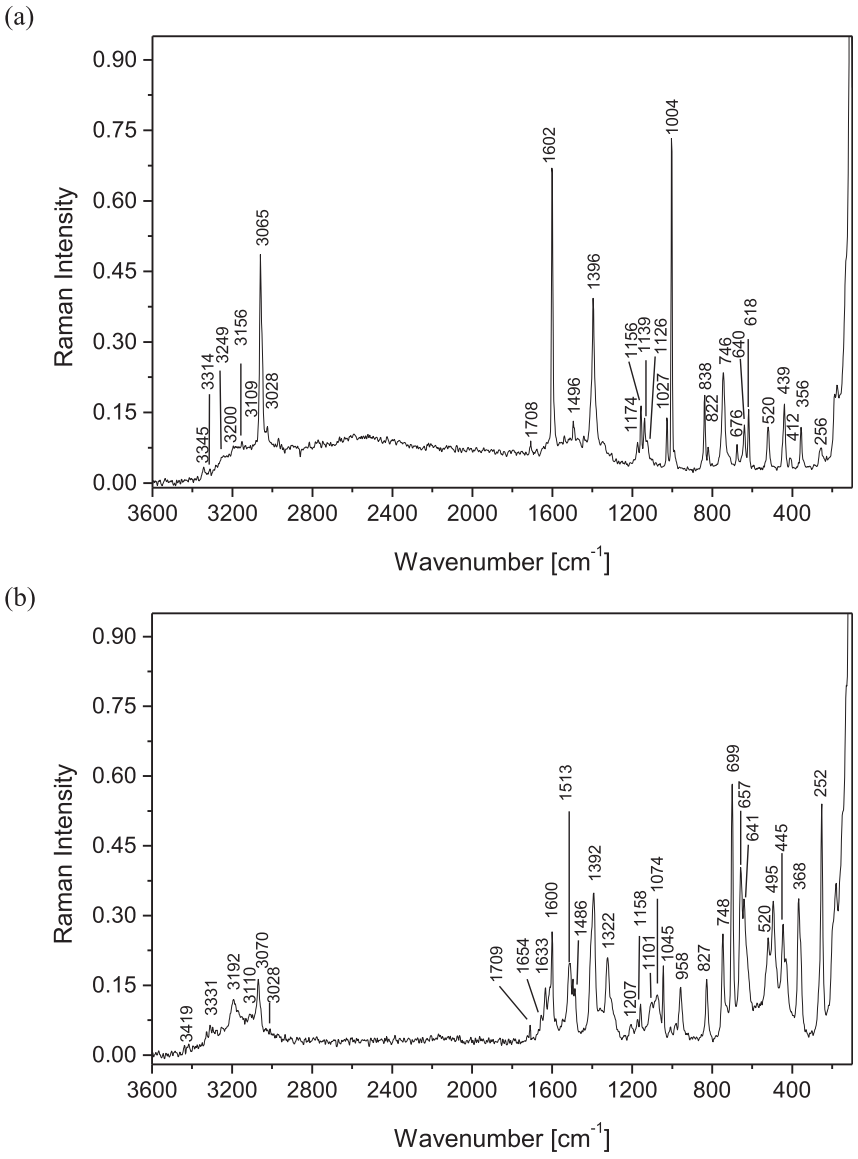


Fig. 6. Raman spectrum of 1-(diaminomethylene)thiouron-1-ium benzoate (a) and bis(1-(diaminomethylene)thiouron-1-ium phthalate trihydrate (b).

protiated compounds are shown in Fig. 6. The title compounds have several functional and skeletal groups such as three NH_2, C═S, C–N–C, N–C–N and N–C–S groups in the cation and one or two COO^- groups and the six-membered aromatic ring in the anions. The bands corresponding to the vibration of these groups were identified with the aid of infrared correlation charts [22]. The IR spectra of neutral 1-(diaminomethylene)thiourea [10 g] and of benzoic acid [23], phthalic acid [24] as well as benzoate(−) and phthalate(2-) [25] will be helpful for assignment of the bands observed in the spectra of the title compounds (Tables 4 and 5). The IR spectrum of protiated 1-(diaminomethylene)thiouron-1-ium benzoate (Fig. 4a) shows medium-strong intensity bands in the spectral range of 3400 and 3000 cm^{-1}. These bands can be attributed to the asymmetric and symmetric stretching of the three NH_2 groups of the 1-(diaminomethylene)thiouron-1-ium cation. These bands, as expected, are shifted in the IR-spectrum of deuterated sample to the spectral region of 2600–2200 cm^{-1} (Fig. 4b). The isotopic ratio between 1.310 and 1.372 points on the vibration anharmonicity. The IR-spectra of protiated and deuterated samples of bis(1-(diaminomethylene)thiouron-1-ium) phthalate trihydrate show similar correlation between the observed $\nu_{asym}(NH_2)$ and $\nu_{sym}(NH_2)$ and $\nu_{asym}(ND_2)$ and $\nu_{sym}(ND_2)$ (Fig. 5a and b). The IR spectra of deuterated analogues (Figs. 4b and 5b), the bands of the protiated compounds with significantly lower intensities are observed. These bands resulting from the equilibrium between the protiated and deuterated analogues and point on the not fully exchange of H to D. The degree of deuterization is estimated to ~80% in **1** and ~90% in **2**. In the Raman spectrum of protiated compounds (Fig. 6) the $\nu(NH_2)$ stretching vibration bands appear in the 3350–3000 cm^{-1} as a very weak once. The Raman spectra exhibit two narrow bands at 3065 and 3028 cm^{-1} in **1** and at 3070 and 3028 cm^{-1} in **2** and they are assigned to C–H stretching of the benzoate and phthalate anions (Table 6). The medium strong intensity band at 1718 cm^{-1} and 1717 cm^{-1} in the IR spectrum of benzoate and phthalate salts, respectively, is assigned to the stretching of imine bond of 1-(diaminomethylene)thiouron-1-ium cation, since it is not observed in the IR spectrum of neutral 1-(diaminomethylene)thiourea [10 g]. Its counterpart is observed at 1708 and 1709 cm^{-1} in the Raman spectrum of benzoate and phthalate salts (Fig. 6). A similar band is observed in the IR-spectrum of some imines and their salts [26]. This assignment of the imine stretching vibration band is confirmed by IR–spectra of deuterated samples, in which the deuterated imine stretching is observed at 1258 cm^{-1} in benzoate and at 1254 cm^{-1} in phthalate (Figs. 4b and 5b, Tables 4 and 5). The isotopic ratio for the band of imine group is equal to 1.366 (for **1**) and 1.369 (for **2**) and points on the almost the same anharmonic vibration. The ν(C═S) band of the 1-(diaminomethylene)thiouron-1-ium cation is observed in the spectral region of 720–710 cm^{-1} in both salts. The ν(C═S) band in the spectrum of several thiourea metal complexes is observed in the range of 715-700 cm^{-1} [21]. The 1-(diaminomethylene)thiouron-1-ium cation contains C–N and the C–N–C, N–C–N skeletal groups and the respective vibrational bands are also observed (Tables 4 and 5).

The assignment of the IR bands of benzoate(−) and phthalate(2-) anions of the samples were made based on the literature [27]. The notation used in the Tables 4 and 5 for benzoate(−) and phthalate(2-) anions for the vibrational modes associated with the benzene ring is commonly used for substituted benzene derivatives and is made by analogy to the notation established for the modes of benzene by Wilson [28]. For benzoate(−) and phthalate(2-) anions the characteristic $\nu(C–C)_{ar}$, $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$ bands are observed in the spectral region of 1620–1380 cm^{-1}, and the β(C–H) and γ(C–H) vibrational bands are observed in the range of

Table 4
FT - IR spectral data for protiated and deuterated analogue of 1-(diaminomethylene)thiouron-1-ium benzoate.

Protiated, ν cm^{-1}	Deuterated, ν cm^{-1}	Assignment	Isotopic ratio
3389m	2540s	$\nu_{asym}(NH_2)/\nu_{asym}(ND_2)$ asym stretch.	1.334
3327s	2498s	$\nu_{asym}(NH_2)/\nu_{asym}(ND_2)$ asym stretch.	1.332
3273s	2465s	$\nu_{asym}(NH_2)/\nu_{asym}(ND_2)$ asym stretch.	1.328
3142m	2351m	$\nu_{sym}(NH_2)/\nu_{sym}(ND_2)$ sym stretch	1.336
3084w	2331m	$\nu_{sym}(NH_2)/\nu_{sym}(ND_2)$ sym stretch	1.323
3057w	2228m	$\nu_{sym}(NH_2)/\nu_{sym}(ND_2)$ sym stretch	1.372
3023w			
broad			
band ~2800	~2200	N–H···O/N–D···O hydrogen bonds	
1718m	1258m	Imine bond stretch.	1.366
1671w			
1618vs	1620s,1596s	8a, 8b (Benzene ν(CC))[a]	
1525w	1553s	$\nu_{asym}(COO^-)$	
1469m	1469s	19a (Benzene ν(CC)) overlapped with ν(CN)	
1389vs	1390s	$\nu_{sym}(COO^-)$	
	1308m	14 (Benzene ν(CC))	
1174w	1174w	9a (Benzene ν(CC))	
1153w	1153w	ν(CN)	
1124w	1123w	ν(CN)	
1068w	1068w	18b (Benzene δ(CH))	
1025w	1025w	18a (Benzene ν(CC))	
1000w	998w		
898w			
838m	837m	$\beta_{sym}(COO^-)$	
745m			
711m	712s	ν(C═S)	
676m	675m	Skeletal C–N–C, N–C–N	
640w		$\tau(NH_2)$, $\omega(NH_2)$	
613w		Skeletal C–N–C, N–C–N	
583w	585w	Skeletal C–N–C, N–C–N	
529w	529w	$\beta_{asym}(COO^-)$	
514w	511w		

vs, very strong; s, strong; m, medium; w, weak.
[a] Notation for the modes of the benzene ring according to Willson [28].

Table 5
FT-IR spectral data for protiated and deuterated analogue of bis(1-(diaminomethylene)thiouron-1-ium) phthalate trihydrate.

Protiated, ν cm^{-1}	Deuterated, ν cm^{-1}	Assignment	Isotopic ratio
3532m	2618w	$\nu_{asym}(OH)/\nu_{asym}(OD)$ (water)	1.349
3431s	2567m	$\nu_{asym}(NH_2)/\nu_{asym}(ND_2)$ asym stretch., overlapped with $\nu_{sym}(OH)$ or $\nu_{sym}(OD)$ (water)	1.337
3401s	2515w	$\nu_{asym}(NH_2)/\nu_{asym}(ND_2)$ asym stretch.	1.352
3263s	2460m	$\nu_{asym}(NH_2)/\nu_{asym}(ND_2)$ asym stretch.	1.326
3157s	2386s	$\nu_{sym}(NH_2)/\nu_{sym}(ND_2)$ sym stretch	1.323
3126s	2360m	$\nu_{sym}(NH_2)/\nu_{sym}(ND_2)$ sym stretch	1.310
3102s	2306m	$\nu_{sym}(NH_2)/\nu_{sym}(ND_2)$ sym stretch	1.345
broad			
band	~2100	N–H···O/N–D···O hydrogen bonds	
~2800	2123m	N–H···O/N–D···O hydrogen bonds	
2725m		O–H···O/O–D···O hydrogen bonds	
2603w		O–H···O/O–D···O hydrogen bonds	
2464w			
2145w			
1717s	1254m	Imine bond stretch.	1.369
1645s	1640s		
1621vs	1600m	8a, 8b (Benzene ν(CC))[a]	
1537vs	1550vs	$\nu_{asym}(COO^-)$	
1466m	1454s	19a (Benzene ν(CC)) overlapped with ν(CN)	
1447s	1447s	ν(CN)	
	1397s,		
1383vs	1383s	$\nu_{sym}(COO^-)$	
1355m	967w	$\delta(NH_2)/\delta(ND_2)$	
1328m	1321w	ν(CN)	
1155m	1155w	9a (Benzene ν(CC))	
1108w	1107w	ν(CN)	
1088m			
859m	858w		
845m			
829m	829w		
772m	772m	$\beta_{asym}(COO^-)$	
730m	722w	ν(C=S)	
691	692m	4 (Benzene ν(CC))	
640w		$\tau(NH_2)$, $\omega(NH_2)$	
624w	624w	Skeletal C–N–C, N–C–N	
579w	582w	Skeletal C–N–C, N–C–N	
521w	520w	$\beta_{asym}(COO^-)$	
482w	483w		

vs, very strong; s, strong; m, medium; w, weak.
[a] Notation for the modes of the benzene ring according to Willson [28].

1360–1000 cm^{-1} and 970–740 cm^{-1}, respectively. The assignment of the characteristic $\nu(C–C)_{ar}$, $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$ bands for phthalate(2-) anion has been supported by theoretical calculation performed by Loring et al. [29]. Since the phthalate salt contains hydrated water molecules, in the IR-spectrum the bands of $\nu_{asym}(OH)$ and $\nu_{sym}(OH)$ are observed as medium bands at 3522 and 3431 cm^{-1} (Fig. 5a), which are shifted to 2618 and 2567 cm^{-1} in IR-spectrum of the deuterated analogue (Fig. 5b). In the Raman spectrum of hydrated compound **2** the stretching vibration of O–H of water are attributed to the weak band at 3419 cm^{-1} (Fig. 6b). The X-ray data reveal that the NH_2 groups of the 1-(diaminomethylene) thiouron-1-ium cation are involved in N–H···O and N–H···S hydrogen bonds. In addition, in the crystal **2** the hydrated water molecules are involved as donors and as acceptors in the $O_{(water)}$–H···$O_{(water)}$ and N–H···$O_{(water)}$ hydrogen bonds. These hydrogen bonds are relatively weak, with the lengths between the 2.721 (1) and 3.078 (2) Å (Table 3). This reveals as a broad band in the range of 3300–2500 cm^{-1} in both protiated samples, which is shifted to ~2200 cm^{-1} in the deuterated analogues.

4. Conclusion

This study confirms the usefulness of 1-(diaminomethylene) thiourea as a building block in the crystal engineering and demonstrates its interaction with benzoic and phthalic acids forming of extended supramolecular hydrogen bonding structures. The $R_2^2(8)$ and $R_2^1(6)$ motifs describe the interaction between the oppositely charged units of the crystals. The hydrogen bonding interactions lead to formation of layered 2D supramolecular structure in 1-(diaminomethylene)thiouron-1-ium benzoate (**1**), whereas in bis(1-(diaminomethylene)-thiouron-1-ium) phthalate trihydrate (**2**) the hydrogen bonding interactions lead to formation of 3D supramolecular network. In crystal **2**, the hydrated water molecules are contributed in the formation with phthalate(2-) anions of O–H···O hydrogen bonding anionic 2D layered substructure. In both crystals are no π–π interactions between the aromatic rings of anions. Comparison of the IR spectra of 1-(diaminomethylene)thiouron-1-ium benzoate and bis(1-(diaminomethylene)-thiouron-1-ium) phthalate trihydrate with the spectra of theirs deuterated analogues shows marked differences in the region of vibrations of the amine groups as well as in the region of N–H···O and O–H···O hydrogen bonds.

Supplementary material

Additional material comprising X-ray powder diffraction patterns of protiated and deuterated samples of 1 and 2 as well as the microscopic images of these two crystals. Full details of the X-ray data collection and final refinement parameters including anisotropic thermal parameters and full list of the bond lengths and angles have been deposited with the Cambridge Crystallographic Data Center in the CIF format as supplementary publications no.

Table 6
Raman spectral data for 1-(diaminomethylene) thiouron-1-ium benzoate (**1**) and bis(1-(diaminomethylene)thiouron-1-ium) phthalate trihydrate (**2**).

1, ν cm^{-1}	2, ν cm^{-1}	Assignment
	3419w	$\nu_a(H_2O)$
3345w	3331w	$\nu_a(NH_2)$ asym stretch.
3314w		$\nu_a(NH_2)$ asym stretch.
3249w	3240sh	$\nu_a(NH_2)$ asym stretch.
3200w	3192w	$\nu_s(NH_2)$ sym stretch. and O–H···O stretch.
3156w		$\nu_s(NH_2)$ sym stretch.
3109w	3110w	$\nu_s(NH_2)$ sym stretch.
3065m	3070m	C–H stretch.
3028w	3028w	C–H stretch.
1708w	1709w	Imine bond stretch.
	1654w	
	1633w	
1602m	1600m	$\nu_{asym}(COO^-)$, N–C–N bend + ring def.
	1513m	
1496w	1486w	N–C–N bend + ring def.
1396m	1392m	$\nu_{sym}(COO^-)$
	1322m	$\delta(NH_2)$
1174w	1207w	
1156w	1158w	ν(C–N), ν(C–C)
1139w		
1126w	1101w	Γ(C–C)
	1074w	
1027w	1045w	ν(C–C)
1004s		
	958w	
838m		
822w	827m	$\beta_{asym}(COO^-)$
746m	748m	ν(C–C), ν(C=S)
	699m	C–C–C def. out of plane of phenol ring
676w	657m	ν(C–C)
640w	641m	$\tau(NH_2)$, $\omega(NH_2)$
618m	610sh	Skeletal C–N–C, N–C–N
520w	520w	$\beta_{asym}(COO)$
	495m	
439m	445m	
412w	414w	
356w	368m	Skeletal C–N–C, N–C–N,
256w	252m	

weak, w; medium, m; strong, s; very, v; shoulder, sh.

CCDC 1409699 and 1409700. Copies of the data can be obtained free of charge on the application to CCDC, 12 Union Road, Cambridge, CB21EZ, UK, (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.molstruc.2015.10.080.

References

[1] (a) G.R. Desiraju, Crystal Engineering. The Design of Organic Solids, Elsevier, Amsterdam, 1989;
(b) J.C. MacDonald, G.R. Whitesides, Chem. Rev. 94 (1994) 2382–2420;
(c) G.R. Desiraju, Angew. Chem. Int. Ed. 46 (2007) 8342–8352.

[2] (a) J.M. Lehn, Supramolecular Chemistry: Concepts and Perspectives, VCH, Weinheim, 1995;
(b) C.B. Aakeröy, Acta Cryst. B53 (1997) 569–586;
(c) D. Braga, Chem. Commun. (2003) 2751–2754;
(d) G.R. Desiraju, Acc. Chem. Res. 35 (2002) 565–573.

[3] (a) B. Moulton, M.J. Zaworotko, Chem. Rev. 101 (2001) 1629–1658;
(b) G.R. Desiraju, J. Am. Chem. Soc. 135 (2013) 9952–9967.

[4] (a) G.R. Desiraju, Chem. Commun. (1997) 1475–1482;
(b) C.B. Aakeröy, N.R. Champness, C. Janiak, CrystEngComm 12 (2010) 22–43.

[5] (a) G.R. Desiraju, Perespectives in Supramolecular Chemistry, vol. 2, Wiley, Chichester, U.K, 1996;
(b) C.B. Aakeröy, P.D. Chopade, C. Gasner, J. Desper, Chem. Commun. 47 (2011) 4688–4690;
(c) O. Altintas, D. Schulze-Suenninghausen, B. Luy, C. Barner-Kowollik, ACS Macro. Lett. 2 (2013) 211–216;
(d) C.T. Seto, G.M. Whitesides, J. Am. Chem. Soc. 115 (1993) 905–916;
(e) J.I. Arenas-Garcia, D. Herrera-Ruiz, K. Mondragón-Vásquez, H. Morales-Rojas, H. Höpfl, Cryst. Growth Des. 12 (2012) 811–824;
(f) G.R.Desiraju, CrustEngComm 5 (2003) 466–467.

[6] (a) G.M. Whitesides, E.E. Simanek, J.P. Mathias, C.T. Seto, D. Chin, M. Mammen, D.M. Gordon, Acc. Chem. Res. 28 (1995) 37–44;
(b) G.R. Desiraju, Angew. Chem. Int. Ed. 34 (1995) 2311–2327;
(c) T. Steiner, Angew. Chem. Int. Ed. 48 (2002) 49–76;
(d) G.J. Perpetuo, J. Janczak, Acta Cryst. C63 (2007) o301–o302;
(e) C.C. Seaton, K. Chadwick, G. Sadig, K. Guo, R.J. Davey, Cryst. Growth Des. 10 (2010) 726–733;
(f) B.A. Blight, C.A. Hunter, D.A. Leigh, H. McNab, P.I.T. Thomson, Nat. Chem. 3 (2011) 244–248;
(g) A.J. Wilson, Nat. Chem. 3 (2011) 193–194;
(h) C.C. Cheng, Y.C. Yen, F.C. Chang, RSC Adv. 1 (2011) 1190–1194;
(i) R. Patra, H.M. Titi, I. Goldberg, Cryst. Growth Des. 13 (2013) 1342–1349.

[7] (a) M.C. Etter, J. MacDonald, J. Bernstein, Acta Cryst. B46 (1990) 256–262;
(b) M.C. Etter, Acc. Chem. Res. 23 (1990) 120–126;
(c) M.C. Etter, J. Phys. Chem. 95 (1991) 4601–4610.

[8] J. Janczak, G.J. Perpetuo, Acta Cryst. C64 (2008) o114–o116.

[9] (a) K. Chakrabaty, S.P.S. Gupta, Indian J. Phys. A57 (1983) 205–209;
(b) K. Chakrabaty, T. Kar, S.P.S. Gupta, Acta Cryst. C46 (1990) 2065–2068;
(c) E. Doxiadi, R. Vilar, A.J.P. White, D.J. Williams, Polyhedron 22 (2003) 2991–2998;
(d) M. Hołyńska, M. Korabik, M. Kubiak, Polyhedron 29 (2010) 530–538.

[10] (a) G.J. Perpétuo, J. Janczak, Acta Cryst. C64 (2008) o264–o268;
(b) J. Janczak, G.J. Perpétuo, Acta Cryst. C64 (2008) o330–o334;
(c) M. Hołyńska, M. Kubiak, Acta Cryst. C64 (2008) o609–o612;
(d) J. Janczak, G.J. Perpétuo, Acta Cryst. C65 (2009) o118–o120;
(e) M. Hołyńska, M. Kubiak, Acta Cryst. C65 (2009) o191–o194;
(f) M. Hołyńska, M. Kubiak, Acta Cryst. C65 (2009) o410–o413;
(g) J. Janczak, G.J. Perpétuo, J. Mol. Struct. 975 (2010) 166–172;
(h) J. Janczak, G.J. Perpétuo, J. Mol. Struct. 988 (2011) 73–81;
(i) G.J. Perpétuo, J. Janczak, J. Mol. Struct. 1007 (2012) 74–80;
(j) G.J. Perpétuo, J. Janczak, J. Mol. Struct. 10541 (2013) 127–138;
(k) G.J. Perpétuo, R.S. Gonçalves, J. Janczak, J. Mol. Struct. 1096 (2015) 74–83;
(l) J. Janczak, Cryst. Growth Des. 15 (2015) 5097–5111.

[11] G.J. Perpétuo, J. Janczak, J. Mol. Struct. 1031 (2013) 14–21.

[12] C.C.D. CrysAlis, CrysAlis Red, Version 171.32.6, Oxford Diffraction Poland, Wrocław, Poland, 2006.

[13] G.M. Sheldrick, SHELXS97, SHELXL97, Programs for Crystal Structures Solution and Refinement, University of Göttingen, Göttingen, Germany, 1997.

[14] K. Brandenburg, H. Putz, DIAMOND Version 3.0, Crystal Impact GbR, Bonn, Germany, 2006.

[15] F.H. Allen, Acta Cryst. B58 (2002) 380–388.

[16] D.R. Johnson, F.X. Powell, W.H. Kirchoff, J. Mol. Spectrosc. 39 (1971) 136–145.

[17] (a) G. Bruno, L. Randaccio, Acta Cryst. B36 (1980) 1711–1712;
(b) D. Feld, M.S. Lahmann, Z. Kristallogr. 157 (1981) 215–231. (c) C.C. Wilson, N. Shankland, A.J. Florence, J. Chem. Soc. Faraday Trans. 92 (1996) 5051–5067;
(d) W. Cai, A. Katrusiak, CrystEngComm 14 (2012) 4420–4424.

[18] O. Ermer, Helv. Chim. Acta 64 (1981) 1902–1909.

[19] G.Y. Bai, H.S. Ning, J. Simpson, X.Y. Qin, N. Li, Acta Cryst. E62 (2006) o4567–o4568.

[20] F.H. Allen, C.H. Bird, R.S. Rowland, P.R. Raithby, Acta Cryst. B53 (1997) 696–701.

[21] F.H. Allen, C.H. Bird, R.S. Rowland, P.R. Raithby, Acta Cryst. B53 (1997) 680–695.

[22] (a) G. Socrates, Infrared Characteristic Group Frequencies, Wiley-Interscience, Chichester, U.K, 1980;
(b) G. Socrates, Infrared, Raman Characteristic Group Frequencies, third ed., Wiley, New York, USA, 2001.

[23] (a) S. Hayashi, N. Kimura, Bulletin of the Institute for Chemical Research, Kyoto University (1966), 44(4), 335–340. (b) I.D. Reva, S.G. Stepanian, J. Mol. Struct. 349 (1995) 337–340;
(c) S.G. Stepanian, I.D. Reva, E.D. Radchenko, G.G. Sheina, Vibr. Spectrosc. 11 (1996) 123–133.

[24] (a) J.F. Arenas, J.I. Marcos, Spectrochim. Acta A36 (1980) 1075–1081;
(b) E.S. Blanca, J.L. Núñez, P. Martinez, J. Mol. Struct. 142 (1986) 45–48.

[25] (a) J.F. Arenas, J.I. Marcos, Spectrochim. Acta A35 (1979) 355–363;
(b) G.B. Deacon, R.K. Phillips, Coord. Chem. Rev. 33 (1980) 227–250;
(c) W. Lewandowski, B. Dasiewicz, P. Koczoń, J. Skierski, K. Dobrosz-Teperek, R. Świsłocka, L. Fuks, W. Priebe, A.P. Mazurek, J. Mol. Struct. 604 (2002) 189–193.

[26] (a) J. Favrot, J.M. Leclercq, R. Roberge, S. Sandorfy, D. Vocelle, Photochem. Photobiol. 29 (1979) 99–108;
(b) J. Favrot, D. Vocelle, C. Sandrofy, Photochem. Photobiol. 30 (1979) 417–421.

[27] G. Varsanyi, Assignments for Vibrational Spectra of 700 Benzene Derivatives, Akademiai Kiado, Budapest, 1972.

[28] E.B. Wilson, Phys. Rev. 45 (1934) 706–714.

[29] J.S. Loring, M. Karlsson, W.R. Fawcett, W.H. Casey, Spectrochim. Acta A57 (2001) 1635–1642.