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Hydrogen-bonding network in the crystal of 1-(diaminomethylene)thiouron-1-ium picrate

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ABSTRACT

The single crystals of 1-(diaminomethylene)thiouron-1-ium picrate were grown using a solution growth technique. The compound crystallises in the centrosymmetric C2/c space group of the monoclinic system. The conformation of the 1-(diaminomethylene)thiouron-1-ium cation is almost planar, while the conformation of the picrate(−) anion is non-planar. Both NO_2 groups linked in ortho positions in relation to the phenolate oxygen are oppositely turned in relation to the ring plane. Arrangement of the oppositely charged components, i.e. 1-(diaminomethylene)thiouron-1-ium cations and picrate(−) anions in the crystal is mainly determined by ionic and hydrogen bonding interactions forming pseudo-one dimensional chains. The compound was also characterised by the FT-IR and Raman spectroscopy. The characteristic bands of the NH_2, NO_2, C=S and C_{ar}—O groups as well as of skeletal groups are discussed.

1. Introduction

Strong O—H···Y and N—H···Y (Y = O, N) hydrogen bonds play an important role in molecular recognition and self-organisation in crystal engineering and biology [1–3]. On the other hand, much weaker interactions like C—H···Y (Y = O, N) hydrogen bonds as well as the interactions between the π-clouds of aromatic rings have been recently recognized as equally important factors determining the organisation of molecules in crystals and have found a broad application in the crystal engineering for the design of new functional materials [4–8].

The commercially available crystalline product described as 2-imino-4-thiobiuret (amidinothiourea) by Aldrich (CAS No. 2114-02-5) is in fact the tautomeric form of 1-(diaminomethylene)thiourea (Scheme 1), as has been identified by X-ray single crystal analysis [9]. Both tautomers are potentially interesting compounds that can be used in the crystal engineering to built up extended frameworks, since they contain complementary arrays of hydrogen bonding sites.

Additionally, both tautomers possess several potential coordination modes, since they can act as *N*,*N*- or *N*,*S*-coordinating ligands and can form several different types of complexes with metal ions. The coordination of the metals by these tautomers is feasible with both neutral and deprotonated (anionic) forms [10–12]. Besides the known Pt and Pd complexes with these tautomers, the 2-imino-4-thiobiuret or 1-(diaminomethylene)thiourea can form salts, since they contain the N atom with lone pair of electrons that can accept the H atom, forming positively charged cations [13–17].

Picric acid (2,4,6-trinitrophenol) is an organic acid, which is used, in the dyeing industry and as an explosive. The presence of three electron withdrawing nitro groups makes it as a good π-acceptor for neutral carrier donor molecule [18–20]. In addition, picric acid is used at human theraphy (treatment of burns, antiseptic and astringent agent) [21]. Several complexes or salts of the picric acid with organic molecules exhibit non-linear optical applications [22].

In the present work, we investigate the crystal structure of 1-(diaminomethylene)thiouron-1-ium picrate by the X-ray diffraction. The compound was also characterized by vibrational (FT-IR and Raman) spectroscopy, and the results are discussed in comparison with the data obtained for the neutral molecule of 1-(diaminomethylene)thiourea.

2. Experimental

All materials were commercially available and used as received. The Fourier transform infrared spectra were recorded from Nujol mulls between 400 and 4000 cm^{-1} on a Bruker IFS 113V FTIR spectrometer at room temperature. Elemental analyses were carried out with a Perkin-Elmer 240 elemental analyzer.

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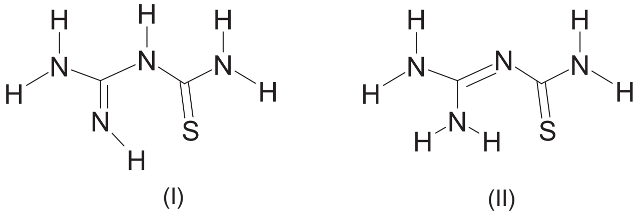


Scheme 1.

2.1. Preparation of 1-(diaminomethylene)thiouron-1-ium picrate

Commercially available 2-imino-4-thiobiuret (amidinothiourea, Aldrich, CAS No. 2114-02-5), which is in fact the tautomeric form 1-(diaminomethylene)thiourea and picric acid (Aldrich, purity of 99%) were added to hot water in a molar proportion of 1:1. When the solution became homogenous it was cooled slowly and kept at room temperature. After several days, transparent yellowish crystals were formed. Anal. Calculated for $C_8H_9N_7O_7S$: C, 27.67; H, 2.60; N, 28.24, O, 32.27 and S, 9.22%. Found: C. 27.54; H, 2.57; N, 28.32; O, 32.33 and S, 9.24%.

2.2. X-ray data collection

X-ray intensity data for the crystal 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 $\Delta\omega = 1.0°$ for each image was used for data collection. The 760 images for six different runs covering over 95% of the Ewald sphere were performed. The unit cell parameters were refined by the least-squares methods on the basis of 1826 reflections. One image was used as a standard after every 40 images for monitoring the crystal stability and data collection, and no correction on the relative intensity variations was necessary. 15,262 reflections (3364 independent, $R_{int} = 0.0231$) were measured up to 57.90° in 2θ. Data collections were made using the CrysAlis CCD program [23]. Integration, scaling of the reflections, correction for Lorenz and polarisation effects and absorption corrections were performed using the CrysAlis Red program [23]. The structure was solved by the direct methods using SHELXS-97 and refined using SHELXL-97 programs [24]. The hydrogen atoms joined to aromatic ring were located in their geometrical positions and refined as riding model with the $U_{iso} = 1.2U_{eq}$ of the C atoms joining H, the other H atoms were located from difference Fourier maps and were refined. The final difference Fourier map showed no peaks of chemical significance. The largest peaks on the final $\Delta\rho$ map were +0.176 and −0.269 eÅ^{-3}. Details of the data collection parameters, crystallographic data and final agreement parameters are collected in Table 1. Visualisation of the structure was made with the Diamond 3.0 program [25]. The geometrical parameters are collected in Table 2.

2.3. Quantum calculations

Ab initio molecular orbital calculations full geometry optimization were performed with the Gaussian98 program package [26]. All calculations were performed by the density functional three-parameter hybrid (B3LYP) methods [27,28] with the 6 – 31 + G* basis set starting from the X-ray geometry. As convergence criterions the threshold limits of 0.00025 and 0.0012 a.u. were applied for the maximum force and the displacement, respectively. The geometrical parameters of the MO-claculated structure are contained in Table 2.

Table 1
Crystallographic data for 1-(diaminomethylene)thiouron-1-ium picrate.

Empirical formula	$C_8H_9N_7O_7S$
Formula weight (g mol^{-1})	347.28
Crystal system, space group	Monoclinic, C2/c (No. 15)
a (Å)	12.698(2)
b (Å)	10.184(2)
c (Å)	21.354(4)
β (°)	101.03(1)
V (Å^3)	2710.4(9)
Z	8
D_{calc}/D_{obs} (g cm^{-3})	1.702/1.70
μ (mm^{-1})	0.293
F(000)	1424
Crystal size (mm)	0.38 × 0.26 × 0.20
Radiation type, wavelength, λ (Å)	Mo Kα, 0.71073
Temperature (K)	295(2)
θ range (°)	3.04 ÷ 28.95
Absorption correction	Numerical, CrysAlis Red [23]
T_{min}/T_{max}	0.8997/0.9476
Reflections collected/unique/observed	15,262/3364/2350
R_{int}	0.0231
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0361
wR (F^2 all reflections)	0.0988
Goodness-of-fit, S	1.004
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	+0.176, −0.269

$wR = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma wF_o^4\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.0577P)^2$ where $P = (F_o^2 + 2F_c^2)/3$.

3. Results and discussion

Good quality single crystals of 1-(diaminomethylene)thiouron-1-ium picrate suitable for the X-ray single crystal analysis were obtained from water solution at room temperature. Fig. 1 shows the molecular structure of the title compound. The X-ray single crystal analysis revealed that the proton of the hydroxyl group of picric acid is transferred to the N1 atom of 1-(diaminomethylene)thiourea forming the 1-(diaminomethylene)thiouron-1-ium cation. These oppositely charged units interact via N—H···O hydrogen bonds forming the cation–anion complex (Fig. 1).

The 1-(diaminomethylene)thiouron-1-ium cation is almost planar (Table 2). This is in contrast to the neutral molecule of 1-(diaminomethylene)thiourea in the crystal [9], where it is non-planar; both arms are turned in opposite directions around the C—N bonds involving the central N1 atom. Thus, in the crystal the conformation of the neutral 1-(diaminomethylene)thiourea is twisted (22.2(1)°), in contrast to the conformation of the 1-(diaminomethylene)thiouron-1-ium cation in the present structure, which is almost planar. A similar non-planar conformation of the cation as for neutral 1-(diaminomethylene)thiourea molecule is observed in all known crystal structure of the 1-(diaminomethylene)thiouron-1-ium salts: chloride, bromide and iodide [13], perchlorate, hydrogen sulfate, dihydrogen phosphate and dihydrogen arsenate [14], nitrate and phosphite [15]. The C1—S1 bond in the cation is longer by ~0.05 Å than the typical double bond as observed in the thioformaldehyde $CH_2C{=}S$ (1.6108(9) Å) [29], which represents 100% double-bond character, and is shorter than the value of ~1.74 Å as observed in the thiolate anions that represents 50% double-bond character [30]. Thus the bond order of the C1—S1 is intermediate between 2 and 1.5. Three C—NH_2 bond distances are in the range 1.309(2) ÷ 1.321(2) Å, are thus shorter than the typical single bond C(sp^2)—NH_2 of 1.341 ÷ 1.363 Å [31]. The C—N bond lengths involving the central N1 atom are significantly longer than the three C—N bonds linking the amine groups (Table 2). The C1—N1—C2 angle of 129.73(12)° is higher than an expected value of sp^2 hybridization due to the steric hindrance of S and NH_2 group. The planarity of the amine groups indicates the sp^2 hybridization of the orbitals on the amine nitrogen atoms with the lone pair of

Table 2
Bond lengths (Å) and angles (°) for 1-(diaminomethylene)thiouron-1-ium picrate.

1-(diaminomethylene)thiouron-1-ium cation	X-ray	ab initio
S1—C1	1.6640(15)	1.662
C1—N2	1.321(2)	1.348
C1—N1	1.3837(18)	1.421
N1—C2	1.3720(18)	1.368
C2—N4	1.3087(19)	1.343
C2—N3	1.3096(18)	1.319
N2—C1—N1	112.87(13)	111.4
N2—C1—S1	121.21(12)	122.9
N1—C1—S1	125.91(11)	125.7
C2—N1—C1	129.73(12)	129.9
N4—C2—N3	122.36(14)	121.3
N4—C2—N1	115.80(13)	117.0
N3—C2—N1	121.84(14)	121.8
S1—C1—N1—C2	0. 9(2)	−9.9
N3—C2—N1—C1	−0.6(2)	6.1
picrate(−) anion		
C3—C4	1.4523(19)	1.475
C4—C5	1.3678(18)	1.378
C5—C6	1.3810(19)	1.406
C6—C7	1.3855(18)	1.406
C7—C8	1.3734(18)	1.378
C3—C8	1.4461(18)	1.475
O1—C3	1.2446(16)	1.257
C4—N5	1.4514(17)	1.449
C6—N6	1.4427(16)	1.426
C8—N7	1.4476(18)	1.449
N5—O51	1.2251(17)	1.265
N5—O52	1.2257(17)	1.282
N6—O62	1.2231(16)	1.282
N6—O61	1.2256(15)	1.282
N7—O71	1.2259(16)	1.282
N7—O72	1.2267(16)	1.265
O1—C3—C8	124.84(13)	124.0
O1—C3—C4	123.78(12)	124.0
C8—C3—C4	111.38(12)	112.0
C5—C4—N5	116.07(12)	116.3
C5—C4—C3	124.91(12)	123.9
N5—C4—C3	119.01(12)	119.8
C4—C5—C6	118.71(12)	119.9
C5—C6—C7	121.32(12)	120.3
C5—C6—N6	119.63(12)	119.9
C7—C6—N6	119.05(12)	119.8
C8—C7—C6	119.15(12)	119.9
C7—C8—C3	124.33(12)	123.9
C7—C8—N7	115.85(12)	116.3
C3—C8—N7	119.82(12)	119.8
O51—N5—O52	122.61(13)	122.5
O51—N5—C4	118.94(13)	119.5
O52—N5—C4	118.43(13)	118.0
O62—N6—O61	122.64(12)	121.9
O62—N6—C6	118.68(12)	119.0
O61—N6—C6	118.68(12)	119.0
O71—N7—O72	122.82(13)	122.5
O71—N7—C8	118.65(12)	118.0
O72—N7—C8	118.51(12)	119.5
C3—C4—N5—O51	36.5(2)	35.0
C3—C8—N7—O72	29.9(2)	34.9

electrons on the *p* orbital that is perpendicular to the plane of the NH$_2$ groups. Additionally, the *p* orbitals of the C, S and N atoms forming the π bond of the C1—S1 and C2—N1 double bonds, are also perpendicular to the plane, therefore the partial delocalisation of the π-bonds over the C—NH$_2$ bonds linking the amine groups, due to symmetry of the *p* orbitals, is possible. Therefore, the double C1=S1 and C2=N1 bonds are longer and the other single C—N bonds linking the amine groups shorter than the typical values of the double C=S and C=N bonds or single C—N bond [32]. A similar correlation between the bond lengths and angles is observed in the gas phase, as predicted for an isolated 1-(diaminomethylene)thiouron-1-ium cation by the density functional theory [13], however the molecular orbital calculation, in contrast to the crystal, results the twisted conformation of the cation (Table 2). Thus the interactions with the picrate counter-ion with the formation of N—H···O hydrogen bonds make the 1-(diaminomethylene)thiouron-1-ium cation almost planar.

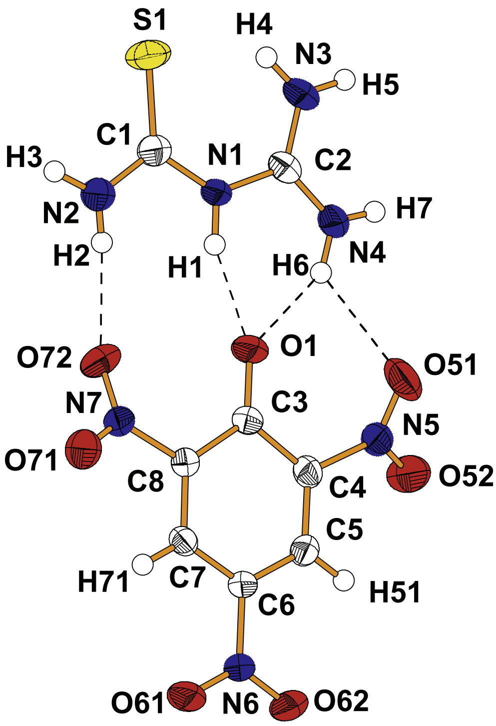


Fig. 1. A view of 1-(diaminomethylene)thiouron-1-ium picrate showing displacement ellipsoids at the 50% probability level and H atoms as a sphere of arbitrary radii. Dashed lines represent the hydrogen bonds.

The asymmetric unit 1-(diaminomethylene)thiouron-1-ium picrate contains the 1-(diaminoethylene)thiouron-1-ium cation and the picrate anion where the hydroxyl group is deprotonated. Deprotonation of the hydroxyl group in picrate anion results in the shortening of the C3—O1 bond (1.2446(18) Å) close to the value of the double C=O bond (1.214–1.224 Å) [31], as well as in the opposite rotation of both NO$_2$ groups attached in orto positions in relation to the carbon atom linking the deprotonated hydroxyl group, due to the repulsive interaction between the negative polarized NO$_2$ groups and the negative charged oxygen (O1). The torsion O51—N5—C4—C3 and O72—N7—C8—C3 angles describing the orientation of the NO$_2$ groups in relation to the plane of the ring are 36.5(2)° and 29.9(2)°, respectively. Thus the conformation of the picrate anion is non-planar and plays a pivotal role in hydrogen bonding with the 1-(diaminomethylene)thiouron-1-ium cation

Table 3
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.91(2)	1.93(2)	2.793(2)	157.3(14)
N2—H2···O72	0.84(2)	2.08(2)	2.909(2)	172.3(19)
N2—H3···O71^{i}	0.89(2)	2.43(2)	3.149(2)	138.0(16)
N2—H3···O62^{ii}	0.89(2)	2.59(2)	3.366(2)	145.9(16)
N3—H4···S1	0.91(2)	2.26(2)	2.978(2)	135.6(15)
N3—H5···O61^{iii}	0.86(2)	2.42(2)	3.084(2)	134.9(15)
N3—H5···O52^{iv}	0.86(2)	2.47(2)	3.198(2)	142.6(16)
N4—H6···O1	0.92(2)	1.94(2)	2.771(2)	148.4(15)
N4—H6···O51	0.92(2)	2.35(2)	3.024(2)	129.6(14)
N4—H7···O51^{iv}	0.78(2)	2.25(2)	3.032(2)	176.6(18)

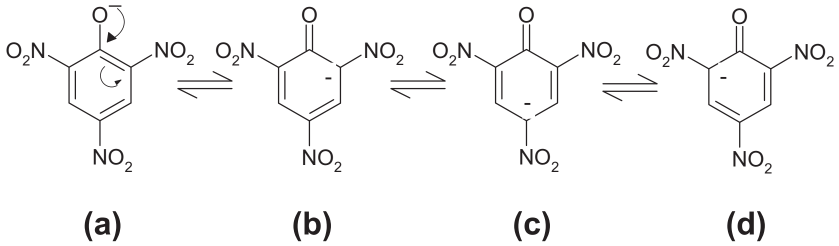
Symmetry code: $i = -x + ½, -y - ½, -z + 1$; $ii = x, -y, z + ½$; $iii = x - ½, -y + ½, z + ½$; $iv = -x, -y + 1, -z + 1$.

and leads to the formation of intermediate N—H···O hydrogen bonds (Table 3). The conformation of the picrate anion is different from the conformation of the picric acid, in which one of two NO_2 groups in orto position is coplanar with the ring due to the formation of intramolecular hydrogen bond with the hydroxyl group [33]. The third NO_2 group joined in para position in relation to the hydroxyl or deprotonated hydroxyl group is coplanar with the ring in both neutral picric acid molecule and deprotonated picrate(−) anion. The orientation of this NO_2 group is stabilised by the intramolecular interaction with the H atoms (O61···H71 and O62···H51). The C—C bonds involving the C atom linking the deprotonated hydroxyl group are significantly longer than the remaining four C—C bonds within the ring (Table 2). The repulsive interactions of the deprotonated oxygen atom O1 with the electron withdraw NO_2 groups attached in the ortho positions in relation to the O1 are responsible for the lengthening of the C3—C4 and C3—C8 bonds as well as for the significant differences between the internal C—C—C angles within the ring. Both C—C—C angles joining the NO_2 groups (C3—C4—C5 and C3—C8—C7) are significantly greater and the C4—C3—C8 angle joining the deprotonated hydroxyl group is significantly smaller than the expected angle for C sp^2 hybridization (Table 2). The partially double in character of C⎓O bond linked the phenolic oxygen as well as the relatively long C3—C4 and C3—C8 bonds can be explained by the resonance structures presented in Scheme 2.

Ab-initio full-optimised molecular orbital calculation performed for an isolated picrate anion shows similar correlation between the bond lengths and distances as found in the crystal (Table 2). However, the small differences between the X-ray and MO calculated values are noticeable but understable if we take into account the interactions with oppositely charged partner in the crystal. The ab initio MO calculations confirm the non-planar conformation of picrate anion observed in the crystal. In the gas phase structure the NO_2 groups attached to the ring in ortho position in relations to deprotonated O1 atom are turned around the C4—N7 and C8—N7 bonds by ~35.0°. The deprotonation of the hydroxyl group (O1) increases the steric effect of the lone electron pairs at O1 and causes the rotation of the ortho NO_2 group. The steric effect of the lone pair of electrons at the O1 atom makes the internal C4—C3—C8 angle significantly smaller than 120° and both O1—C3—C4 and O1—C3—C8 angles greater than 120° and is in agreement with the valence shell electron pair repulsion model (VSEPR), according to which the lone-pair of electrons occupies a wider region as the bonding pair [34]. In addition, the steric effect of the lone pair of electrons at O1 together with the interaction the negatively polarized NO_2 groups are responsible for the angle distortions within the ring from 120° as expected for C sp^2 hybridization.

The oppositely charged units, i.e. 1-(diaminomethylene)thiouron-1-ium cation and picrate anion interact via N—H···O hydrogen bonds forming hydrogen bonded cation–anion complex. These cation–anion complexes related by an inversion interact via additional N—H···O hydrogen bonds forming pseudo-one dimensional hydrogen bonded polymer (Fig. 2). In the crystal, the hydrogen-bonded polymers are located almost parallel to the (212) and (2-12) planes forming layers parallel to the (0 0 1) crystallographic plane (Fig. 3). Within one layer the almost planar 1D-polymers interact via π–π clouds between the aromatic six-membered ring of picrate anions and the planar 1-(diaminomethylene)thiouron-1-ium cations in which the π electrons of the double C1—S1 and C2—N1 bonds are delocalized over the whole cation. The distance between the ring of picrate anion and the mean plane of the 1-(diaminomethylene)thiouron-1-ium cation are 3.56 Å indicating on the weak π–π interactions that stabilise the three dimensional structure.

The FT-IR and Raman spectra of the 1-(diaminomethylene)thiouron-1-ium picrate are show in Figs. 4 and 5, respectively. Bands corresponding to vibration of the functional groups were identified with the aid of infrared correlation charts [35,36]. In addition the spectra were compared with the spectra of 1-(diaminomethylene)thiourea and picric acid that are also illustrated in Figs. 4 and 5. The title compound has several functional and skeletal groups



Scheme 2.

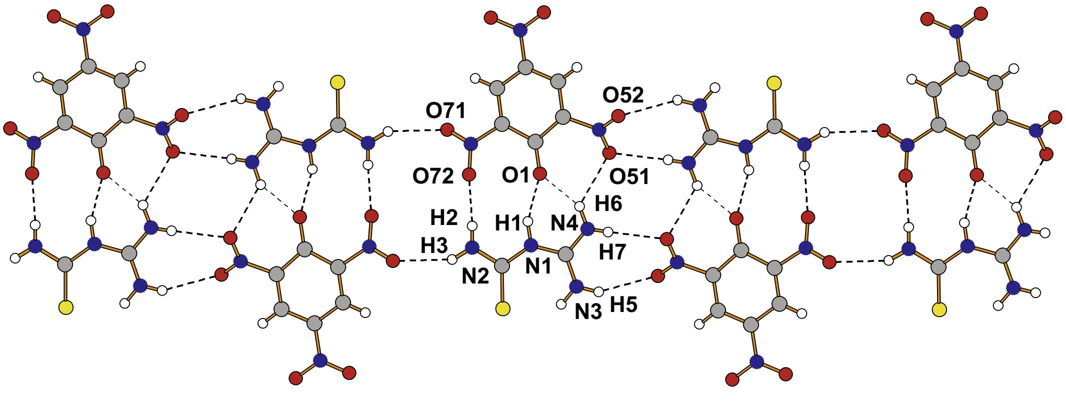


Fig. 2. Pseudo-one dimensional hydrogen bonded chain of 1-(diaminomethylene)thiouron-1-ium picrate.

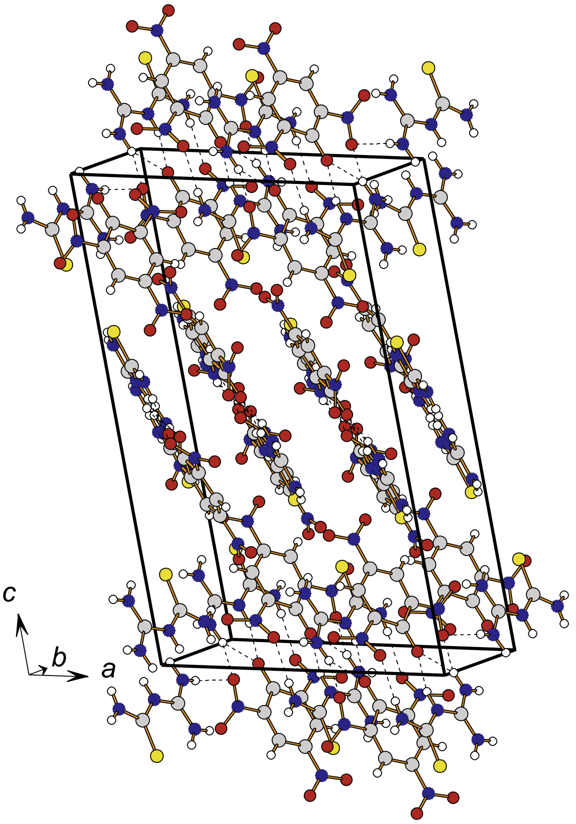


Fig. 3. Molecular packing of 1-(diaminomethylene)thiouron-1-ium picrate in the unit cell.

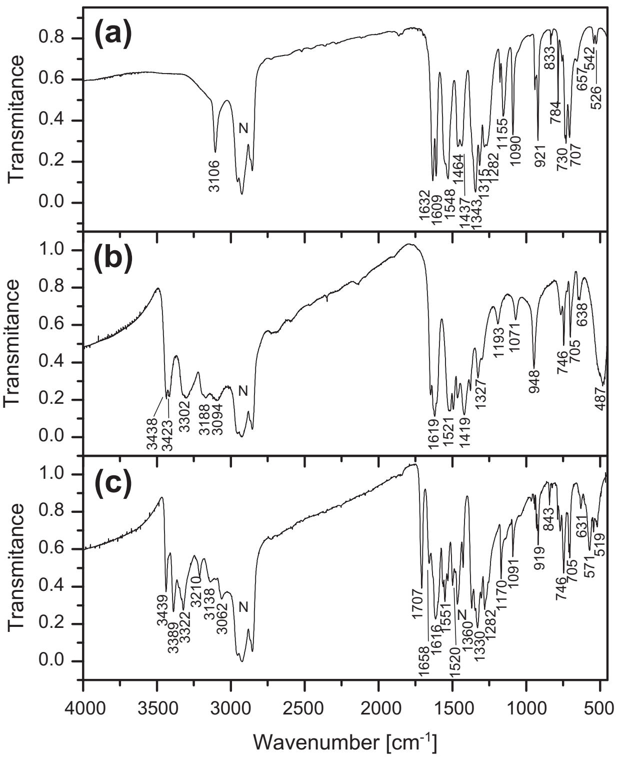


Fig. 4. Room temperature FTIR spectra of picric acid (a), 1-(diaminomethylene)thiourea (b) and 1-(diaminomethylene)thiouron-1-ium picrate (c).

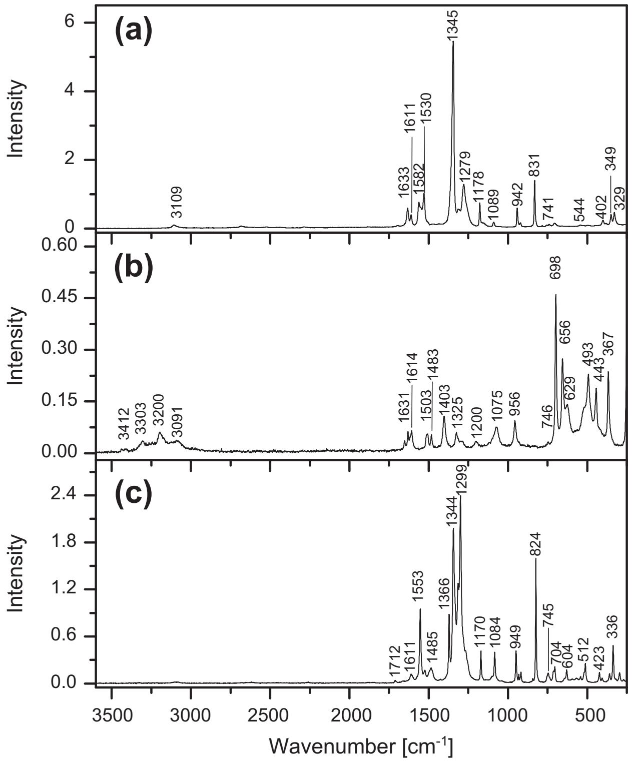


Fig. 5. Room temperature Raman spectra of picric acid (a), 1-(diaminomethylene)thiourea (b) and 1-(diaminomethylene)thiouron-1-ium picrate (c).

such as three NH_2, C=S, C—N—C, N—C—N and N—C=S in the cation and three NO_2, C_{ar} —NO_2, C_{ar}—O^- and six-membered skeletal aromatic ring in the anion. A careful inspection of the IR spectrum shows three medium-strong intensity bands in the range between 3439 and 3322 cm^{-1} that can be attributed to the asymmetric stretching of the three NH_2 groups of 1-(diaminomethylene)thiouron-1-ium cation and three weaker bands in the spectral region of 3210–3062 cm^{-1} attributed to the symmetric stretching of the NH_2 groups. The strong intensity band at 1616 cm^{-1} in IR with weak intensity Raman counterparts at 1611 cm^{-1} is attributed to NH_2 asymmetric deformation mode. The X-ray data reveal that all NH_2 groups of the 1-(diaminomethylene)thiouron-1-ium cation are involved in nine N—H···O hydrogen bonds with bond lengths ranging from ~2.77 to ~3.37 Å (the distance between donor and acceptor). This is reflected in the infrared spectrum as a broad band in the range 3300–2750 cm^{-1}. Additionally, the broad band in the range of 1400–1100 cm^{-1} overlapped with the ν_{sym} stretching NO_2 points to the presence of the N—H···O hydrogen bonds. The vibrations of the N—C(S)—N group in the thiourea are observed in the range between 1480 and 1130 cm^{-1}. The band at 1419 cm^{-1} observed in the IR spectrum of 1-(diaminomethylene)thiourea (Fig. 4b) corresponds to the 1414 cm^{-1} of thiourea, and is a contributions of the NH_2 rocking and N—C—N vibrations [37]. The ν(C=S) in thiourea is observed at 730 cm^{-1}, while in several thiourea metal complexes the ν(C=S) band is observed in the range 715–700 cm^{-1} [32]. Vibration of the C=S bond is coupled with the bending vibration of the picrate(−) ring and the band is observed at the 705 cm^{-1}. Similar band is also observed in other picrate slats.

The picrate being the 2,4,6-trinitrophenolate(−) anion has characteristic bands of the deprotonated phenol, the bands of three NO_2 groups and the bands of the six-membered aromatic ring. As can be seen from Fig. 4a, the band at 3106 cm^{-1} observed in the spectrum of pure picric acid disappeared in the spectrum of picrate (Fig. 5c). The relatively low wavenumber (3106 cm^{-1}) points to the presence of the intramolecular O—H···O interaction that was confirmed by the X-ray single crystal analysis of picric acid [33]. Thus the absence of the O—H stretching confirms a proton transfer from picric acid to 1-(diaminomethylene)thiourea molecule with the formation of the picrate(−) anion and 1-(diaminomethylene)thiouron-1-ium cation. Apart from this, the other functional groups existing in the picrate(−) anion are the nitro NO_2 groups and the phenolic C_{ar}—O^- group. The C—C ring stretching modes are observed as expected at 1616, 1488 and 1467 cm^{-1} (Table 4) in the spectrum of 1-(diaminomethylene)thiouron-1-ium picrate as well as in the spectrum of picric acid. The C—H bending mode is assigned as a medium intensity band at 824 cm^{-1} in Raman spectrum and at 843 cm^{-1} in the IR spectrum of the salt. Picric acid absorbs strongly at 1345 cm^{-1} as a result of symmetric stretching vibration of nitro groups. The acid also displays two closely spaced bands at 1562 and 1530 cm^{-1} due to the NO_2 asymmetric stretching vibration mode. Besides the mentioned above bands, in the present crystal, the Raman spectrum exhibits, a band at 1368 cm^{-1} and a very strong band at 1299 cm^{-1}; both are not observed in the spectrum of pure picric acid. Comparing the conformation of the picrate(−) anion in the 1-(diaminomethylene)thiouron-1-ium picrate with the conformation of molecule of pure picric acid [33] it should be stated that they are different. Both NO_2 groups of the picrate(−) anion are linked to the ring in orto positions in relation to the phenolic oxygen (CO^-) and are oppositely rotated in relation to the plane of the ring, whereas in picric acid only one of two orto NO_2 group is rotated, the other is coplanar with the aromatic ring due to the formation of the intramolecular O—H···O hydrogen bond between the hydroxyl group and the oxygen atom of the NO_2 group. This conformation together with the intermolecular N—H···O hydrogen bonds leads to the splitting of the ν_{sym} (NO_2) band. The band at 1282 cm^{-1} in the IR spectrum is assigned to phenolic O vibration, $\nu(C_{ar}$—O) mode as was assigned in several picrate salts [38–43]. The appearance of a medium intensity band at 1285–1255 cm^{-1} in the metal picrate complexes is attributed to the $\nu(C_{ar}$—O) mode due to the coordination of phenolic oxygen after deprotonation [21]. For the lanthanide picrates, this band is observed at ~1275 cm^{-1} [44–46]. The origin and nature of the relatively strong and narrow band at 1707 cm^{-1} in the IR spectrum of the salt (Fig. 4c), which is not observed in pure picric acid (Fig. 4a) and pure 1-(diaminomethylene)thiourea (Fig. 4b) are not clear. In the 1:1 and 2:1 complexes of N-methylmorpholine betaine with picric acid the band in this spectral region (~1730 cm^{-1} in the complex of 1:1 and 1727 cm^{-1} in the complex of 2:1) has been attributed to the $\nu(C_{ar}$=O) of picrate(−) anion [47]. However, as shown by the X-ray analysis in both complexes the C—O bond lengths of 1.260(5) and 1.221(6) Å [47] are very close to the value of 1.2446(16) Å observed in the present structure as well as in other picrate salts [48]. Since in the spectra of several picrate salts the band above 1700 cm^{-1} is not observed [38–46], therefore the band at 1707 cm^{-1} can not be assigned to the phenolic oxygen vibration. Nevertheless, this band could be ascribed to the stretching of an imine bond of the 1-(diaminomethylene)thiouron-1-ium cation, since a similar band is observed in some imines and their picrate slats [49]. The stretching vibration of an imine bond frequency goes from ~1667 cm^{-1} in some free imines to ~1704 cm^{-1} in their picrates [49]. The observed frequencies and their assignments are listed in Table 4.

Table 4
FT IR and Raman spectral data for 1-(diaminomethylene)thiouron-1-ium picrate.

Infrared, ν (cm^{-1})	Raman, ν (cm^{-1})	Assignment
3439m		NH_2 asym stretch.
3389s		NH_2 asym stretch.
3322s		NH_2 sym stretch.
3210w		NH_2 sym stretch.
3138w		N—H
	3082vw	N—H
3062m		N—H
	2618vw	Overtones and combination bands
	2262vw	Overtones and combination bands
	1712vw	Imine bond stretch.
1707s		Imine bond stretch.
1658m		NH_2 asym def.
1616vs		NH_2 asym def.
	1611w	
1551s	1553m	ν(C—N) and NO_2 asym stretch.
1520m	1522w	ν(C—N) and NO_2 asym stretch.
1498m		ν(C—C) ring stretch.
	1485w	ν(C—C) ring stretch.
1467s		ν(C—C) ring stretch. overlapped with Nujol
	1366m	ν(C—O)
1360s		NO_2 sym stretch. overlapped with Nujol
	1344vs	NO_2 sym stretch.
1330vs		NO_2 sym stretch.
	1299vs	NO_2 sym stretch.
1282s		Phenolic O
1170m	1170m	
1091	1084m	C—N stretch.
	948m	C—C stretch.
919m		C—C stretch.
843m		NO_2 def.
	824s	NO_2 def., C—H def.
746m	745w	$\omega(NO_2)$
705m	705w	C=S stretch. overlapped with δ(ring)
631w		
	604	
571m		C—C=O def.
519w		
	512w	C—C—C—C ph ring def.
	336m	C—C—C—C ph ring def.

vs, very strong; s, strong; m, medium; w, weak.

4. Conclusion

The single crystals of 1-(diaminomethylene)thiouron-1-ium picrate were grown using a solution growth technique. The 1-(diaminomethylene)thiouron-1-ium cation is planar. This is in contrast to the neutral molecule of 1-(diaminomethylene)thiourea in the crystal as well as in other known crystals of 1-(diaminomethylene)thiouron-1-ium salts, in which the conformation is non-planar. In the picrate(−) anion both orto NO_2 groups in relation to the deprotonated hydroxyl group are oppositely turned in relation to the six-membered aromatic ring, due to the repulsive interaction between the negatively charged phenolic oxygen and the oxygen atoms of NO_2 group. Deprotonation of the picric acid leads to disappearance of the O—H stretching vibration band at 3106 cm^{-1} (observed in picric acid, Fig. 4a) and to appearance of the phenolic O stretching vibration band at 1170 cm^{-1} (observed in the salt, Fig. 4c). In the crystal, nine N—H···O hydrogen bonds exist, which are manifested in the IR spectrum as a broad band between the 3300 and 2750 cm^{-1} and in the range of 1400–1100 cm^{-1}. These bands overlapped with the ν_{sym} stretching NO_2 as well as with the N—C(S)—N skeletal group of the cation and with the skeletal aromatic ring of picrate anion. An arrangement of the oppositely charged components, i.e. 1-(diaminomethylene)thiouron-1-ium cations and picrate(−) anions in the crystal is mainly determined by the ionic and hydrogen bonding interactions forming pseudo-one dimensional chains.

5. Supplementary material

Additional material comprising 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. CCDC 767502. 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).

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